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SYNTHESIS AND APPLICATION OF HELICENE-BASED N-HETEROCYCLIC CARBENE LIGANDS

Ph.D. Thesis

Supervisor: RNDr. Ivo Starý, CSc.

Prohlášení:

Prohlašuji, že jsem závěrečnou práci zpracovala samostatně a že jsem uvedla všechny použité informační zdroje a literaturu. Tato práce ani její podstatná část nebyla předložena k získání jiného nebo stejného akademického titulu.

V Praze, 16.9.2020

Podpis

The Thesis was worked out at the Institute of Organic Chemistry and Biochemistry, v.v.i., Academy of Sciences of the Czech Republic, from 2014 to 2020.

"I hereby declare that I have done this Thesis independently while noting all resources used, as well as all co-authors."

Prague, 16 September 2020

Signature.....

I hereby declare that Isabel Gay Sánchez contributed significantly to all scientific publicatons that are part of this dissertation. She performed experiments and took part in their planning; she interpreted results and participated in manuscript writing. Her contributions to the individual publications are quantified below.

1. Synthesis of Racemic, Diastereopure, and Enantiopure Carba- or Oxa[5]-, [6]-, [7]-, and [19]helicene (Di)thiol Derivatives.

J. Nejedlý, M. Šámal, J. Rybáček, I. G. Sánchez, V. Houska, T. Warzecha, J. Vacek, L. Sieger, M. Buděšínský, L. Bednárová, P. Fiedler, I. Císařová, I. Starý, I. G. Stará. *J. Org. Chem.* **2020**, *85*, 248–276. –10%

2. Oxahelicene NHC Ligands in the Asymmetric Synthesis of Nonracemic Helicenes.

I. G. Sánchez, M. Šámal, J. Nejedlý, M. Karras, J. Klívar, J. Rybáček, M. Buděšínský, L. Bednárová, B. Seidlerová, I. G. Stará, I. Starý. *Chem. Commun*. **2017**, *53*, 4370–4373. –50%

Prague, 16 September 2020

Signature.....

Dr. Ivo Starý

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When I arrived to Czech Republic more than ten years ago I would have never guessed what a personal and intellectual adventure this journey was going to be. Thank you all!

SUMMARY

The aim of my PhD Thesis was to explore the potential of helically chiral N-heterocyclic carbene (NHC) ligands in asymmetric catalysis. Helicenes and helicene-like molecules are inherently chiral. Their application in this field has been rather limited. To date, only a few examples of enantiopure helically chiral NHCs have been described in the literature.

Using a well-established method based on the diastereoselective metal catalysed [2+2+2] cycloisomerisation of centrally chiral triynes as the key step, I have synthesised a series of optically pure 2*H*-pyran based penta- and hexahelicenes bearing an amino group on the terminal benzene ring. The triynes were prepared by a sequence of Sonogashira and Mitsunobu coupling reactions using the commercially available (*S*)-but-3-yn-2-ol as the source of chirality. The resulting aminooxa[5]- and aminooxa[6]helicenes were then converted into the corresponding 1,3-disubstituted imidazolium salts, from which, upon deprotonation, the helically chiral N-heterocyclic carbenes were generated.

To evaluate the performance of the new helically chiral ligands, the enantioselective Ni^0-catalysed [2+2+2] intramolecular cycloisomerisation of prochiral triynes to nonracemic dibenzohelicenes was chosen as a model reaction. All the synthesised imidazolium salts provided, in the presence of a Ni^0 species and a base, highly active Ni^0-NHC complexes. In general, symmetrical imidazolium salt precursors provided higher enantiomeric excess than their unsymmetrical analogues, reaching with the symmetrical imidazolium salts up to 59% *ee* for dibenzo[6]helicene and 74% *ee* for dibenzo[7]helicene. These encouraging results prompted the introduction of bulky substituents onto the helical backbone in order to increase steric congestion around the metal centre and thus enforce the higher level of enantioselectivity. Oxahelicenes bearing a chlorine atom at different positions provided access to a small library of such ligands *via* Suzuki-Miyaura coupling. The stereochemical outcome of the new set of helically chiral NHC ligands ranged from 40% *ee* up to 66% *ee* for dibenzo[6]helicene and reached even 86% *ee* in case of dibenzo[7]helicene.

Although the novel helically chiral ligands show great promise in the enantioselective nickel catalysed [2+2+2] cycloisomerisation, further modification of the helical backbone hand in hand with molecular modelling is required in order to extend the substrate scope and improve

the existing level of enantioselectivity by understanding better the mechanism of chirality transfer.

SOUHRN

Cílem mé disertační práce bylo prozkoumat možnosti využití helikálně chirálních N-heterocyklických karbenových (NHC) ligandů v asymetrické katalýze. Inherentně chirální heliceny a jejich analogy byly dosud v této oblasti využity jen v omezené míře. Do současnosti bylo publikováno jen několik málo příkladů helikálně chirálních NHC ligandů.

Obecná metoda diastereoselektivní [2+2+2] cyklotrimerizace centrálně chirálních triynů byla využita jako klíčový krok při přípravě opticky čistých 2*H*-pyranových penta- a hexahelicenů nesoucích aminoskupinu na koncovém benzenovém kruhu. Příslušné triyny byly připraveny pomocí Sonogashirovy a Mitsunobuovy reakce s využitím komerčně dostupného (*S*)-but-3-yn-2-olu jakožto centrálně chirálního stavebního bloku. Výsledné heliceny byly následně převedeny na odpovídající 1,3-disubstituované imidazoliové soli, z nichž byly deprotonací generovány požadované helikálně chirální N-heterocyklické karbeny.

Enantioselektivní [2+2+2] cykloizomerizaci katalyzovanou komplexy nulmocného niklu jsem pak využila jako modelovou reakci k ověření efektivity nově připravených helikálně chirálních ligandů. Výchozími látkami pro tyto testovací reakce byly prochirální aromatické tryiny, jejichž cyklizací vznikaly neracemické dibenzoheliceny. Všechny připravené imidazoliové soli poskytly v přítomnosti báze a vhodné sloučeniny niklu vysoce aktivní Ni^0-NHC komplexy. Použití symetrických prekurzorů helikálních NHC ligandů vedlo v případě modelové reakce obecně k vyšším enantiomerním nadbytkům než v případě jejich nesymetrických analogů. Enantiomerní nadbytky těchto reakcí dosahovaly až 59% *ee* při syntéze dibenzo[6]helicenu a až 74% *ee* v případě dibenzo[7]helicenu. Při použití Suzukiho-Miyaurovy reakce byla z oxahelicenů nesoucích atom chloru v různých polohách připravena malá knihovna ligandů obsahujících objemné substituenty na periferii helicenového skeletu. Aplikace těchto helikálních NHC ligandů vedla ke vzniku dibenzo[6]helicenu v enantiomerním nadbytku 40% *ee* až 60% *ee* a dibenzo[7]helicenu v nadbytku až 86% *ee*.

Bylo ukázáno, že nově připravené helikálně chirální NHC ligandy se vyznačují slibnou aktivitou při enantioselektivní [2+2+2] cykloizomerizaci. Pro další zvýšení enantioselektivity (a rozšíření použitelnosti helikálních NHC ligandů) je však nutné prozkoumat vliv dalších strukturních modifikací helicenového skeletu. Využití

molekulového modelování by také mohlo přispět k lepšímu porozumění mechanismu přenosu chirality a efektivnímu designu helikálních NHC ligandů.

LIST OF ABBREVATIONS

Ac	acetyl
Ad	adamantyl
acac	acetylacetonate
APCI	atmospheric pressure chemical ionization
aq.	aqueous
b	broad
[bdmim]BF_4	1-butyl-2,3-dimethylimidazolium tetrafluoroborate
BSA	*N,O*-bis(trimethylsilyl)acetamide
BINAP	(2,2′-bis(diphenylphosphino)-1,1′-binaphthalyl)
BINOL	1,1′-bi-2-naphthol
Boc	*tert*-butyloxycarbonyl
Boc_2O	di-*tert*-butyl dicarbonate
n-Bu *or* Bu	*normal* butyl
CD	circular dichroism
CSD	Cambridge Structural Database
cod	1,5-cyclooctadiene
COSY	correlation spectroscopy
Cp	cyclopentadienyl
CP	circularly polarised
CP-OLEDs	circularly polarised organic light-emitting diode
CPL	circularly polarised luminescence
d	doublet
dba	dibenzylideneacetone
de	diastereomeric excess
DFT	density functional theory
DIAD	diisopropyl azodicarboxylate
DMAP	4-(dimethylamino)pyridine
dr	diastereomeric ratio
ee	enantiomeric excess

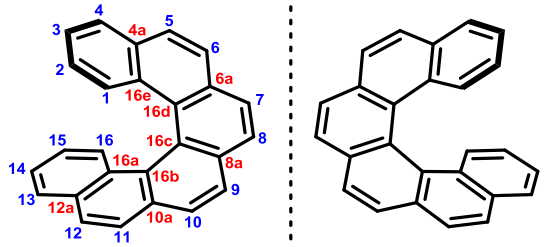
e.g.	for example
EI	electron impact
equiv.	equivalent
ESI	electrospray ionization
fum	dimethyl fumarate
HPLC	high performance liquid chromatography
IPc*	(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethyl-bicyclo[3.1.1]-heptan-3-yl
IR	infrared spectroscopy
i-Pr	isopropyl
IUPAC	International Union of Pure and Applied Chemistry
KHMDS	potassium bis(trimethylsilyl)amide
l-CPL	left circularly polarised light
m	multiplet (NMR) *or* medium (IR)
m-CPBA	*meta*-chloroperoxybenzoic acid
Me	methyl
Mes	mesityl
MOM	methoxymethyl
Mp	melting point
MS	mass spectrometry
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
Ph	phenyl
Piv	pivalate
ppm	parts per million
q	quartet
QUINAP	1-(2-diphenylphosphino-1-naphthyl)isoquinoline
rac	racemic
RCM	ring-closing metathesis
r-CPL	right circularly polarised light
RI-DFT	resolution of identity density functional theory
ROM-CM	ring opening metathesis-cross metathesis

rt	room temperature
s	singlet (NMR) *or* strong (IR)
sh	shoulder
t	triplet
TADDOL	α,α,α',α'-tetraaryl-2,2,disubsituted 1,3-dioxolane-4,5-dimethanol
TAPA	2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid
TBAF	tetra-n-butylammonium fluoride
t-Bu	*tert*-butyl
TEP	Tolman electronic parameter
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin-layer chromatography
TIPS	triisopropylsilyl
TMS	trimethylsilyl
Tol	*para*-tolyl
TS	transition state
μW	microwave reactor
UV/VIS	ultraviolet-visible spectroscopy
$\%V_{bur}$	percent buried volume
vb	very broad
vs	very strong
VAPOL	2,2′-diphenyl-(4-biphenanthrol)
vs	versus
w	weak

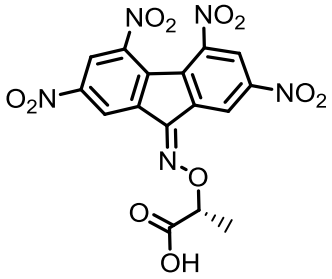
CONTENTS

1 INTRODUCTION

Helicenes are *ortho*-fused polycyclic aromatic or heteroaromatic systems consisting of four or more fused rings.[1,2] A strong steric repulsion between the terminal parts of the helicene molecules drives them from planarity to adopt a helical shape. Accordingly, they are inherently chiral despite the lack of chiral centres. The chirality is denoted with regard to the sense of the twist, *P* for a right-handed helix, or *M* for a left-handed helix (**Figure 1**).[3] Generally, in a carbohelicene series, the *P* enantiomers are dextrorotatory (exhibiting positive specific rotation), whereas the *M* enantiomers are laevorotatory (exhibiting negative specific rotation).[4] The IUPAC nomenclature for this type of compounds became easier by the introduction of the name [n]helicene ([6]helicene or hexahelicene **1** for phenanthro[3,4-*c*]phenanthrene[5]), where [n] denotes the number of *ortho*-fused rings in the helical backbone of the molecule.



(+)-(*P*)-[6]helicene-**1** (-)-(*M*)-[6]helicene-**1**



(-)-TAPA-**2**

Figure 1 Structures of [6]helicene enantiomers and (–)-TAPA

Since the discovery of helicenes by Meisenheimer and Witte in 1903,[6] these screw-shaped molecules have attracted the attention of chemists. A turning point in this field was in 1956 when Newman and Lednicer synthesised [6]helicene **1** for the first time. In this case, (–)-TAPA **2** (**Figure 1**) was used to resolve the racemic mixture of the helicene by means of diastereoselective complexation and crystallisation.[5] This achievement kindled an ever-growing interest in the field of helicene chemistry.

Helicenes, especially in their enantiopure forms, show very interesting geometric, electronic and chiroptical properties and therefore are potentially applicable in enantioselective catalysis,[7–9] molecular recognition,[10,11] organic electronics and photonics,[12,13] chiral materials,[14] and self-assembly.[15,16] However, versatile and efficient synthetic and resolution methods needed to be developed in order to enable all those applications.

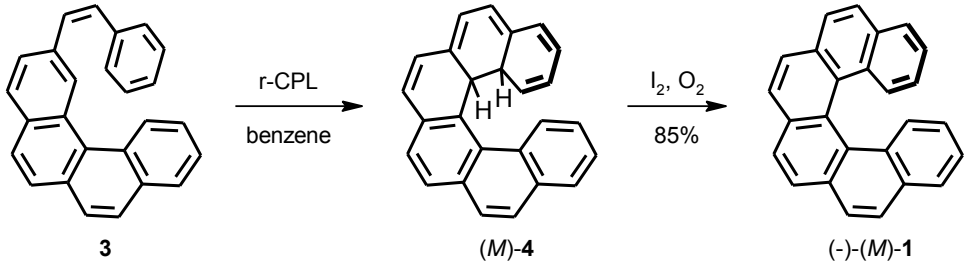
A historical method for obtaining enantiomerically pure or enantioenriched helicenes was described by Martin *et al*. for [6]-, [7]-, [8]- and [9]helicene that is based on spontaneous conglomerate crystallisation and crystal-picking.[17,18] However, this method is very laborious and relies on a serendipitous formation of conglomerate. Nowadays, high performance liquid chromatography (HPLC) on a chiral stationary phase is commonly used to resolve racemic mixtures.[19–21] Nevertheless, this technology has its drawbacks, such as the cost of the equipment or the requirement of good solubility in appropriate solvents. Frequently used alternatives include separation of diastereoisomeric derivatives, salts or complexes by means of crystallisation or chromatography.[22–24] Ultimately, optically pure or enriched helicenes/heterohelicenes can be obtained in sufficient amounts *via* asymmetric synthesis.

1.1 ASYMMETRIC SYNTHESIS OF NONRACEMIC HELICENES

1.1.1 Asymmetric photocyclisation

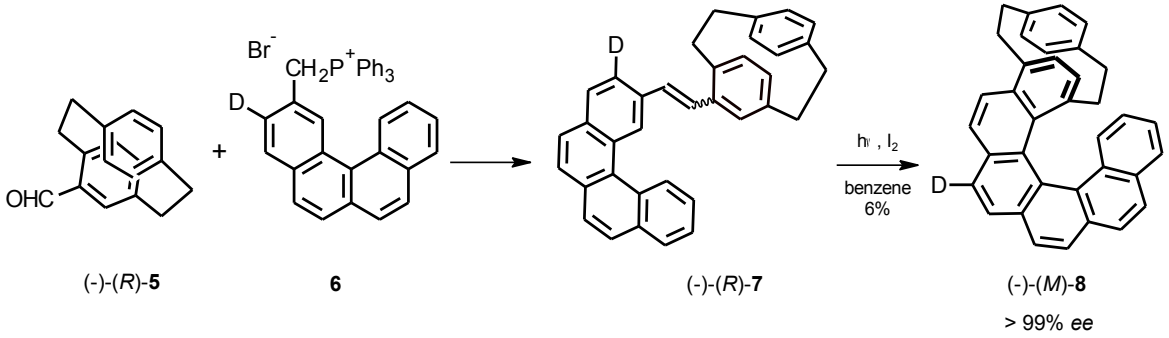
In the early 70's, Kagan and co-workers applied the right or left circularly polarised light (r-CPL or l-CPL) for the enantioselective synthesis of [6]helicene **1**.[25] In this particular case, the stilbene derivative **3** was irradiated for 6 h in the presence of iodine as oxidant to form [6]helicene **1**, which was slightly enantioenriched in favour of the (-)-(*M*)-isomer

(**Scheme 1**). Although a high yield of [6]helicene **1** was obtained, just a very small enantiomeric excess (≤0.2% *ee*) was observed. This pioneering work was then elaborated by Buchardt,[26–28] Stegemeyer and Goedicke,[29] and others, but not with much success. Following a similar idea, Cuppen and Laarhoven tried an asymmetric photocyclisation using chiral solvents for the chirality transfer, obtaining 0.2 – 2.0% *ee*.[30] Even very low *ee*'s can be measured for helicenes due to their very high optical rotations, which increase with the number of fused rings (*e.g.* $[\alpha]_{579}^{25}$ for (*M*)-[7]-, [8]- and [9]helicenes are: –5900, –6900 and –8100, respectively).[18]



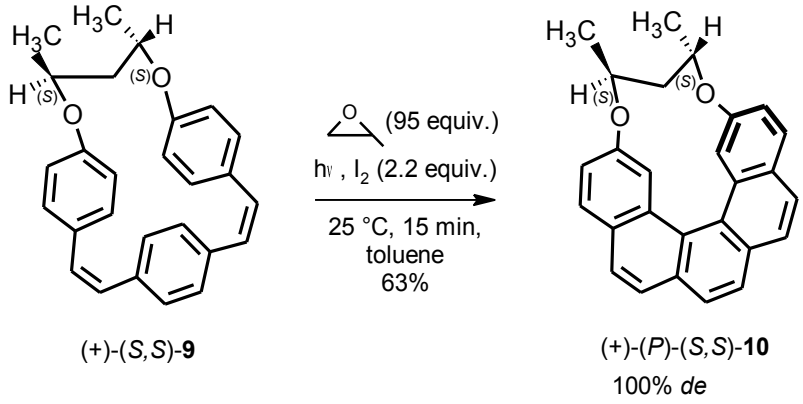
Scheme 1 Asymmetric photocyclisation using right circularly polarised light

Martin and Wynberg *et al*. were the first to combine planar and helical chirality to drive a diastereoselective asymmetric photocyclisation (**Scheme 2**).[31] The optically pure aldehyde (–)-(*R*)-**5** was reacted with ylide generated from the phosphonium salt **6** which led to (–)-(*R*)-**7**. Due to the steric repulsion, the oxidative photocyclodehydrogenation produced exclusively (–)-(*M*)-**8**.



Scheme 2 Diastereoselective asymmetric photocyclisation

A different approach was explored by Marinetti and co-workers, who introduced a chiral tether to lock the conformation of the photocyclisation precursor (+)-(*S,S*)-**9** (**Scheme 3**). After irradiation, a single diastereoisomer (+)-(*P*)-(*S,S*)-**10** was obtained albeit in moderate yield.[32]

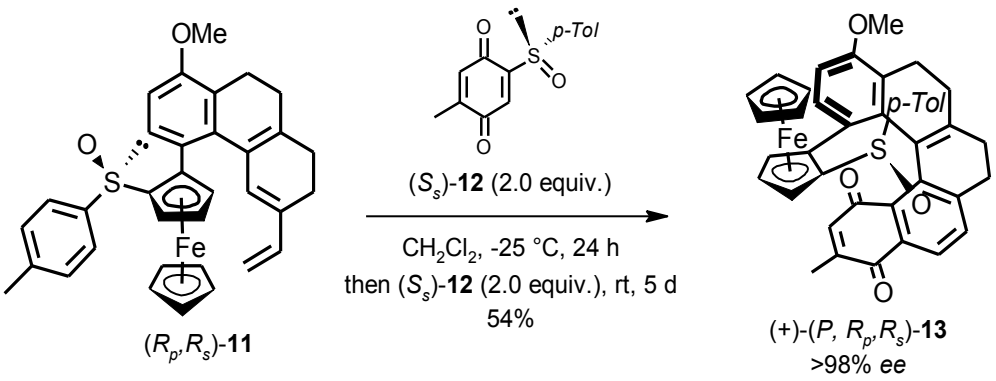


Scheme 3 Chiral tether locking conformation for photocyclisation

1.1.2 Asymmetric Diels-Alder reaction

In the 90's, the development of helicene chemistry was boosted by Katz and co-workers who reported a double thermal Diels-Alder reaction between divinyl arenes and benzo-1,4-quinone that produced carbohelicenes bearing quinone moieties at both ends of the

skeleton.[33] Carreño and co-workers, inspired by the initial work of Katz, developed an asymmetric alternative to this approach leading to nonracemic helicene bisquinones using (*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone as a chiral dienophile.[34–40] Recently, the same authors extended their methodology by using sulfinylferrocenyl **11** and sulfinyl *p*-benzoquinone **12** in asymmetric Diels-Alder reaction to obtain four stereoisomers of **13** which contains elements of helical, planar and central chirality (**Scheme 4**).[41]

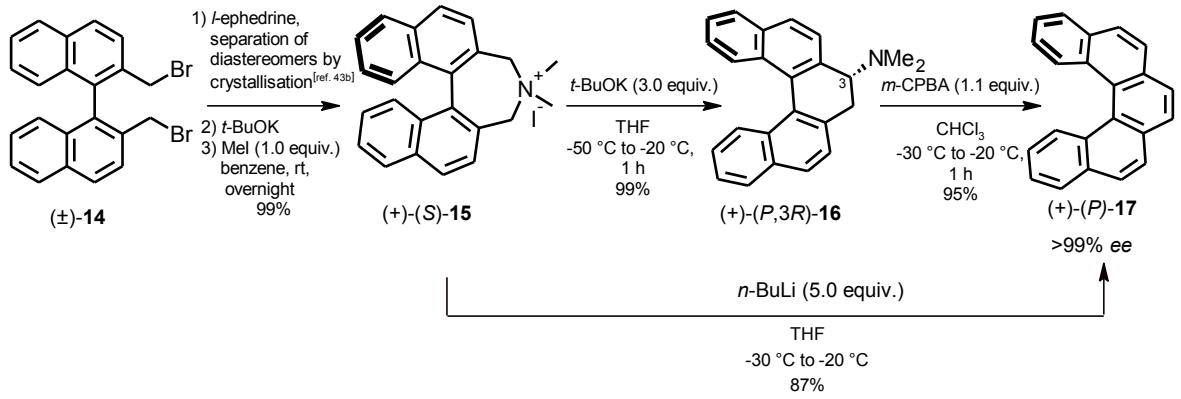


Scheme 4 Asymmetric domino Diels-Alder / pyrolytic sulfoxide elimination / aromatisation to obtain (+)-(*P*,R_p,R_s)-**13**

1.1.3 Synthesis of helicenes from axially chiral biaryl precursors

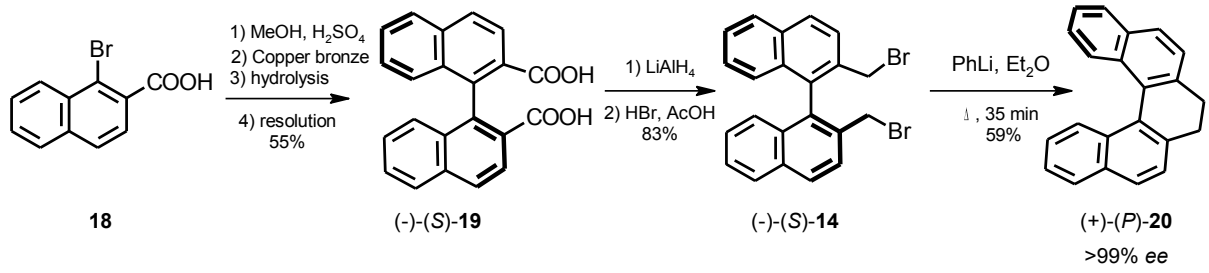
In an early publication by Závada, Stará and Starý, while studying the nucleophilic cleavage of cyclic axially chiral quaternary ammonium salts (easily accessible from 2,2'-bis(bromomethyl)-1,1'-binaphthalene **14**), it was described that treatment of **15** with lithium pyrrolidide or *n*-butyllithium did not lead to the product of ring cleavage but, instead, [5]helicene **17** was isolated.[42] Following this unexpected result Závada *et al.* presented an enantioselective synthesis of [5]helicene **17**. Stevens rearrangement of the dihydroazepinium salt (+)-(*S*)-**15**,[43a,b] furnished (+)-(*P*)-**17**.[44] The use of potassium *tert*-butoxide at temperatures from -50 to -20 °C in THF afforded the optically pure (+)-(*P*,3*R*)-**16**, which upon elimination of the amine moiety (assisted by base or mediated by *m*-CPBA) provided

the enantiopure [5]helicene (+)-(*P*)-**17** (**Scheme 5**). An excess of *n*-butyllithium at -30 °C in THF provided in one pot the optically pure [5]helicene (+)-(*P*)-**17**.



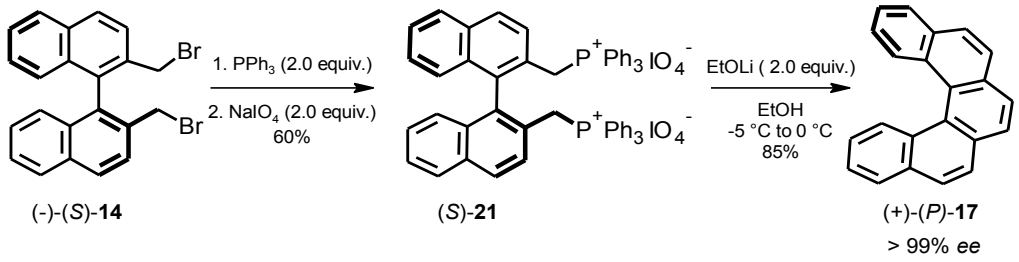
Scheme 5 Stevens rearrangement and amine elimination forms nonracemic [5]helicene

Alternatively, the axial-to-helical chirality transfer can be done *via* benzylic-type coupling. Turner, Hall and Howlett synthesised 7,8-dihydro-[5]helicene **20** using a Wurtz-type benzylic coupling from nonracemic 2,2'-bis(bromomethyl)-1,1'-binaphthyl **14** with phenyllithium (**Scheme 6**).[45] Gingras and Dubois prepared the opposite enantiomer using similar approach starting from the commercially available (–)-(*R*)-1,1'-binaphthalene-2,2'-diol bistriflate.[46]



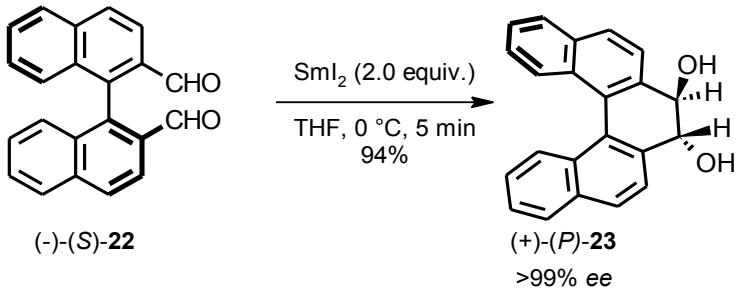
Scheme 6 Wurtz-type benzylic coupling towards nonracemic dihydro[5]helicene

Bestmann and Both converted binapthyl dibromide (–)-(*S*)-**14** into (*S*)-bisphosphonium periodate **21** that in the presence of lithium ethoxide formed (+)-(*P*)-**17** (**Scheme 7**).[47a,b]



Scheme 7 Nonracemic [5]Helicene by oxidation of a binapthyl bisphosphonium salt

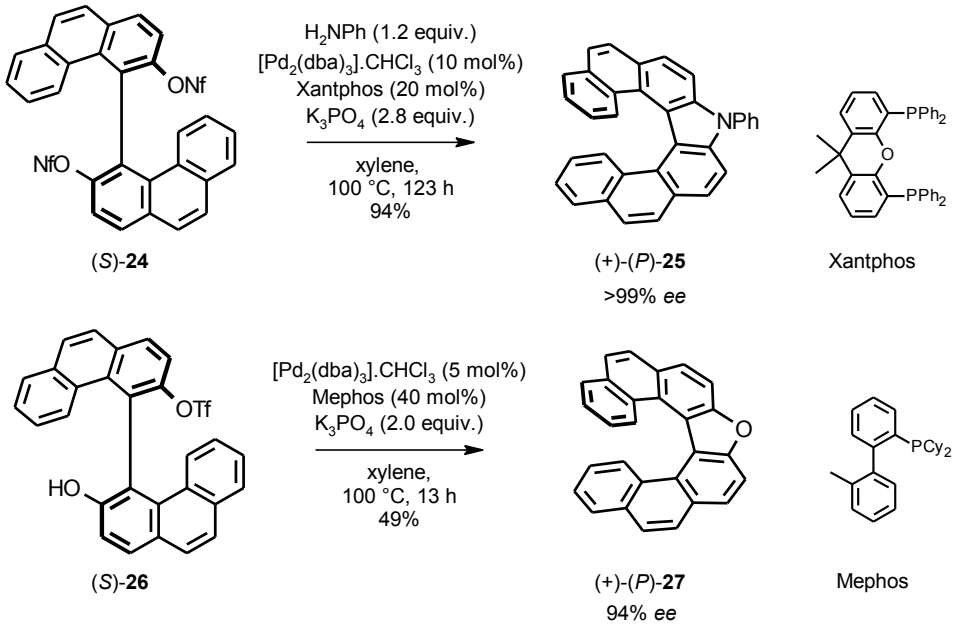
Suzuki *et al*. demonstrated another way of transforming axially chiral precursors into helicenes by means of pinacol-type coupling (**Scheme 8**). The authors treated the optically pure (–)-(*S*)-1,1'-binaphthyl-2,2'dicarboxaldehyde **22** with samarium(II) iodide, which afforded *trans*-diequatorial (+)-(*P*)-7,8-dihydroxy-7,8-dihydro[5]helicene **23**.[48]



Scheme 8 Pinacol-type coupling towards (+)-(*P*)-7,8-dihydroxy-[5]helicene

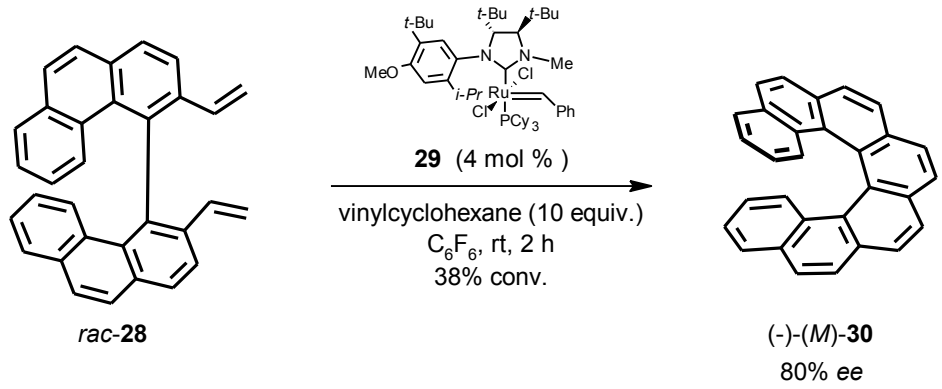
Nozaki *et al*. reported on the palladium catalysed synthesis of aza- and oxa[7]helicenes in moderate to good yields and high enantiopurity (**Scheme 9**).[49] The optically pure axially chiral precursors (*S*)-**24** and (*S*)-**26** were prepared from the racemic 4,4'-biphenanthryl-3,3'-diol by the separation of its diastereoisomeric (1*S*)-10-camphorsulfonates. A double *N*-arylation of primary amine transformed (*S*)-**24** into (+)-(*P*)-**25** in 94% yield with >99% *ee*.

The precursor (*S*)-**26** was transformed into (+)-(*P*)-**27** *via* intramolecular O-arylation. In order to prevent 80% loss of enantiomeric excess, which take place otherwise under the reaction conditions, the reaction time was shortened in this case.



Scheme 9 Palladium catalysed C-O or C-N arylation towards nonracemic heterohelicenes

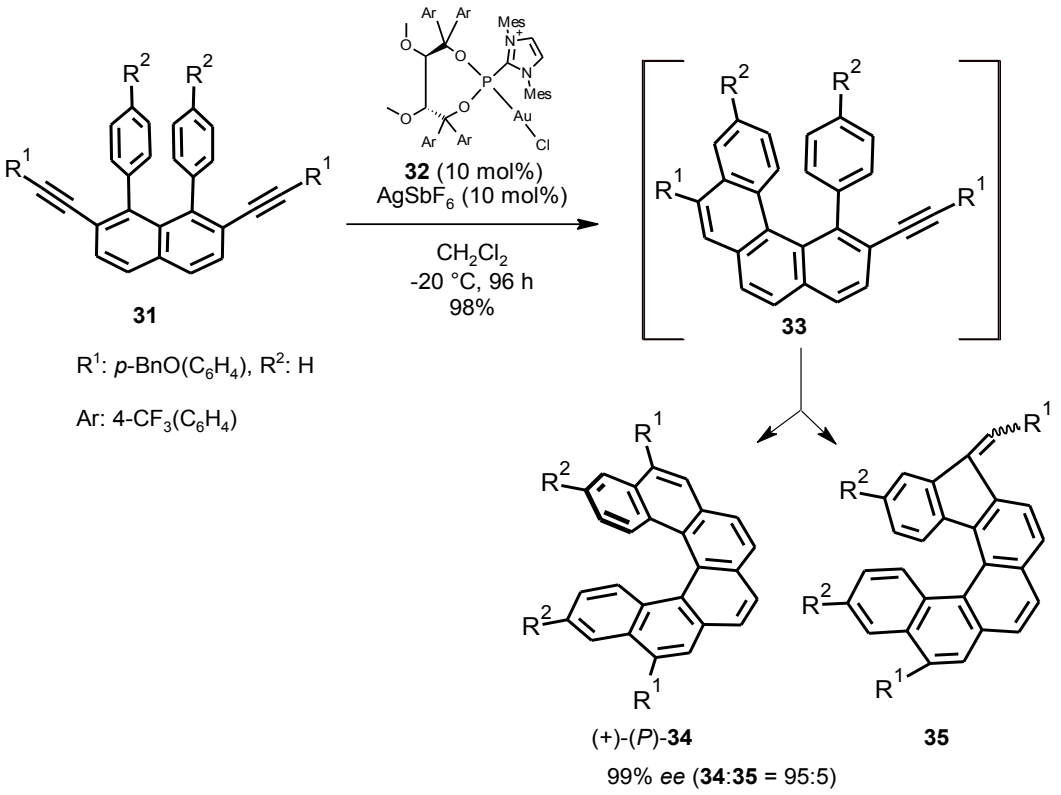
Collins and co-workers introduced a new way of the synthesis of racemic helicenes using ring-closing olefin metathesis (RCM).[50] Later on, they reported on the asymmetric synthesis of (–)-(*M*)-[7]helicene **30** by the kinetic resolution of *rac*-**28** by means of asymmetric olefin metathesis using the chiral Ru complex **29** as a catalyst. Enantioselectivity up to 80% *ee* at 38% conversion was achieved when hexafluorobenzene was used as a solvent and vinylcyclohexane as an additive (**Scheme 10**).[51]



Scheme 10 Synthesis of helicenes by a Ru-catalysed asymmetric olefin metathesis

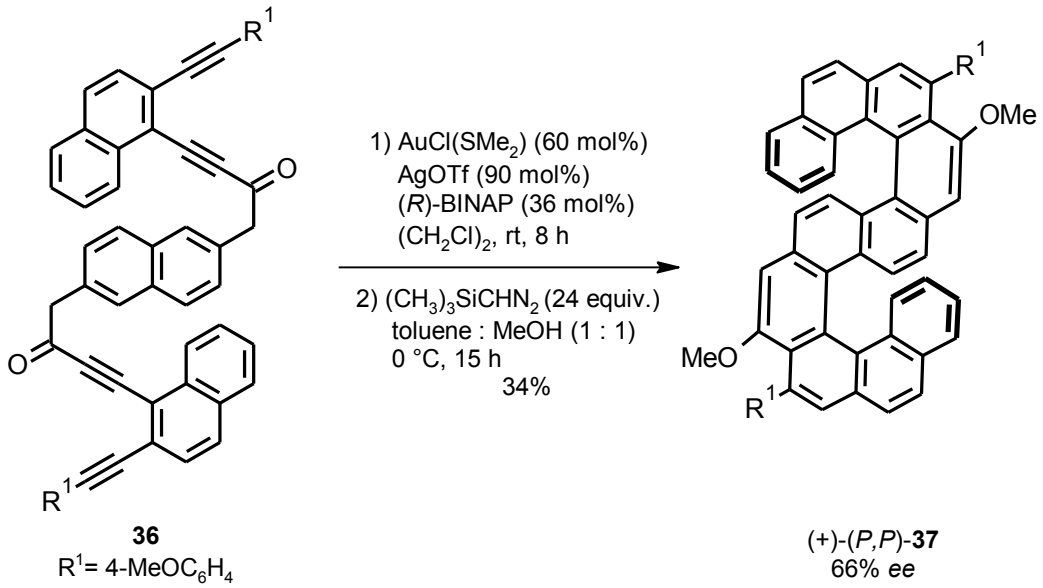
1.1.4 Enantioselective synthesis by intramolecular hydroarylation

Alcarazo *et al*. recently synthesised a series of substituted [6]helicenes using novel TADDOL-derived chiral cationic phosphonites in the intramolecular gold catalysed hydroarylation of diynes.[52,53] This approach led to a small portfolio of new helicenes with good regioselectivity of **34**:**35** up to 99:1 as well as good enantioselectivities 63-99% *ee* (**Scheme 11**).



Scheme 11 Synthesis of helicenes by Au-catalysed enantioselective intramolecular hydroarylation

Lately, Tanaka *et al*. has also applied the gold catalysed intramolecular hydroarylation for the synthesis of [6]helicenes and double [6]helicenes.[54] This methodology was applied to several substrates achieving up to 74% *ee* for [6]helicene derivatives and up to 66% *ee* for the double [6]helicene (+)-(*P,P*)-**37**, as a single diastereoisomer (**Scheme 12**). For the first time, enantioselective synthesis of double helicenes was accomplished. Moreover, the double [6]helicene (+)-(*P,P*)-**37** exhibited relatively large circularly polarised luminescence (CPL) ($|g_{lum}| = 1.5\text{-}2.7\times10^{-3}$).



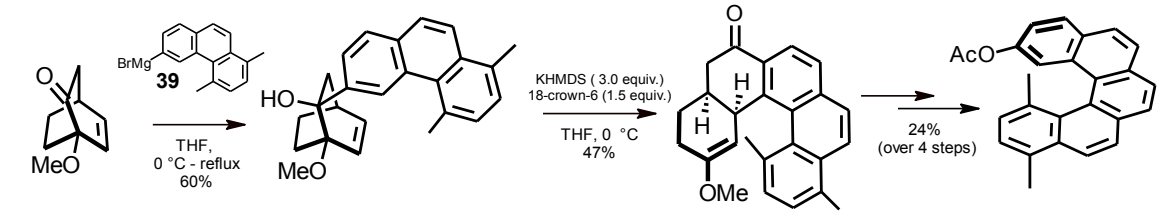
36
R^1= 4-$MeOC_6H_4$

(+)-(*P,P*)-**37**
66% *ee*

Scheme 12 Asymmetric synthesis of double[6]helicene *via* Au-catalysed intramolecular hydroarylation

1.1.5 Asymmetric anionic oxy-Cope rearrangement

A new approach to the synthesis of nonracemic [5]helicenes was explored by Karikomi and co-workers. Optically pure bicyclic ketone (–)-(1*R,*4*S*)-**38** (>98% *ee*) obtained by an enzymatic resolution was first reacted with Grignard reagent **39** and the resulting alcohol (1*R,*2*S,*4*S*)-**40** underwent aromatic oxy-Cope rearrangement to form [5]helicene derivative (4a*S*,14d*R*)-**41**. Finally, (+)-(*P*)-**42** (>98% *ee*) was obtained after four steps with no loss of optical purity over the whole process (**Scheme 13**).[55] In addition, (–)-(*M*)-**42** was accessible starting from the enantioenriched (+)-(1*S*,4*R*)-**38**.



(-)-(1*R*,4*S*)-**38**
> 98% *ee*

(1*R*,2*S*,4*S*)-**40**

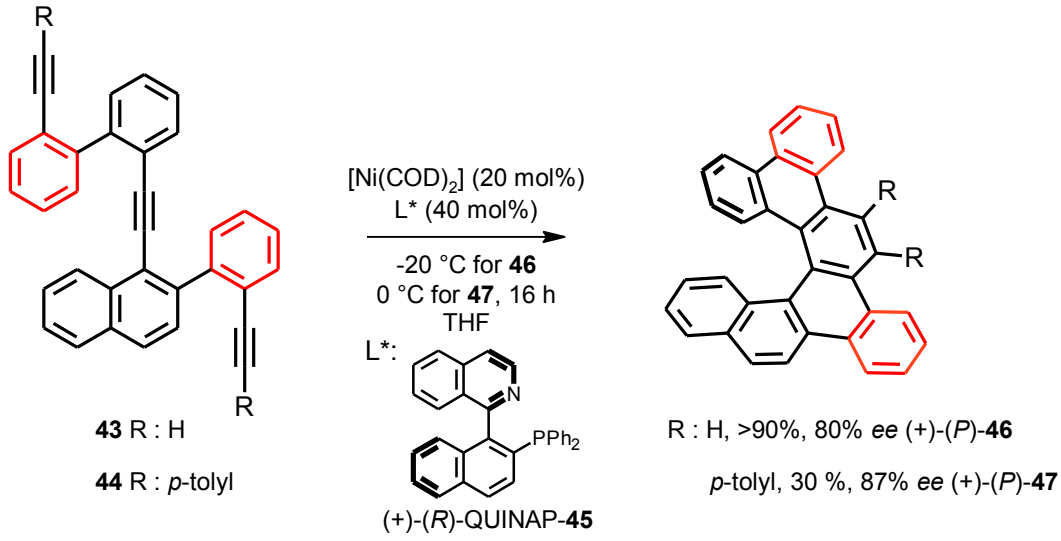
(1a*S*,14d*R*)-**41**

(+)-(*P*)-**42**
> 98% *ee*

Scheme 13 Asymmetric anionic oxy-Cope towards [5]helicene

1.1.6 Asymmetric [2+2+2] cycloisomerisation of alkynes

An atom-economic approach to building helicenes by the transition metal catalysed [2+2+2] cycloisomerisation of triynes was introduced by Stará and Starý *et al*.[56,57] Later on, Stará and Starý *et al*. developed an asymmetric version leading to dibenzo[5]-, dibenzo[6]- and dibenzo[7]helicenes (**Scheme 14**). The key triynes **43** and **44** were synthesised using sequentially Sonogashira and Suzuki-Miyaura couplings and the final helicenes were obtained after cyclisation using Ni^0 catalyst with a chiral ligand.[58] With the optically pure (+)-(*R*)-QUINAP-**45** as a chiral ligand, enantiodiscrimination took place and nonracemic helicenes were obtained in up to 87% *ee*. Their optical purity could be further increased by means of recrystallisation to reach >99% *ee*. Recently, Tanaka *et al*. followed the same strategy to prepare dibenzo[7]helicenes with up to 99% *ee* using a Rh^I/(*R*)-BINAP catalytic system in the asymmetric [2+2+2] cycloisomerisation.[59]



Scheme 14 Enantioselective [2+2+2] cycloisomerisation towards dibenzo[6]helicene

Stará and Starý *et al.* devised also a general method for the synthesis of optically pure heterohelicenes *via* diastereoselective synthesis.[60] In the present study, the equilibrium energies and barriers to epimerisation of the two pairs of diastereoisomers of oxa[5]helicene (*M,R,R*)- and (*P,R,R*)-**48** and **49** were investigated using DFT calculations. For a derivative with hydrogen atoms on the central benzene ring, the stereoisomer (*P,R,R*)-**48** was found to be only 0.2 kcal mol^{-1} more stable than (*M,R,R*)-**48**. In contrast, substitution of the central benzene ring with tolyl groups increased the energy difference between the (*M,R,R*)- and (*P,R,R*)-**49** diastereoisomers to 9.2 kcal mol^{-1}, with (–)-(*M,R,R*)-**49** diastereoisomer being more stable (**Figure 2**).

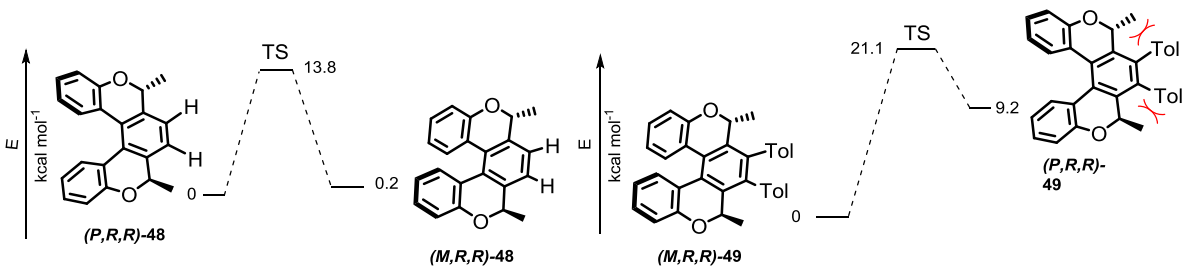
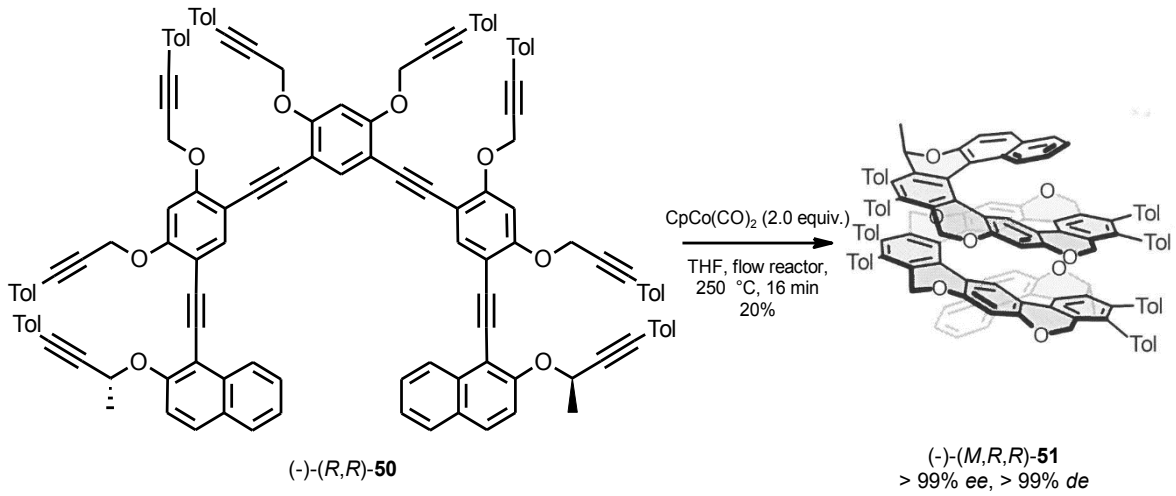


Figure 2 The relative equilibrium free energies and barriers to epimerisation of (*P,R,R*)/(*M,R,R*)-**48** and (*M,R,R*)/(*P,R,R*)-**49** calculated by DFT (B3LYP/cc-pVTZ)

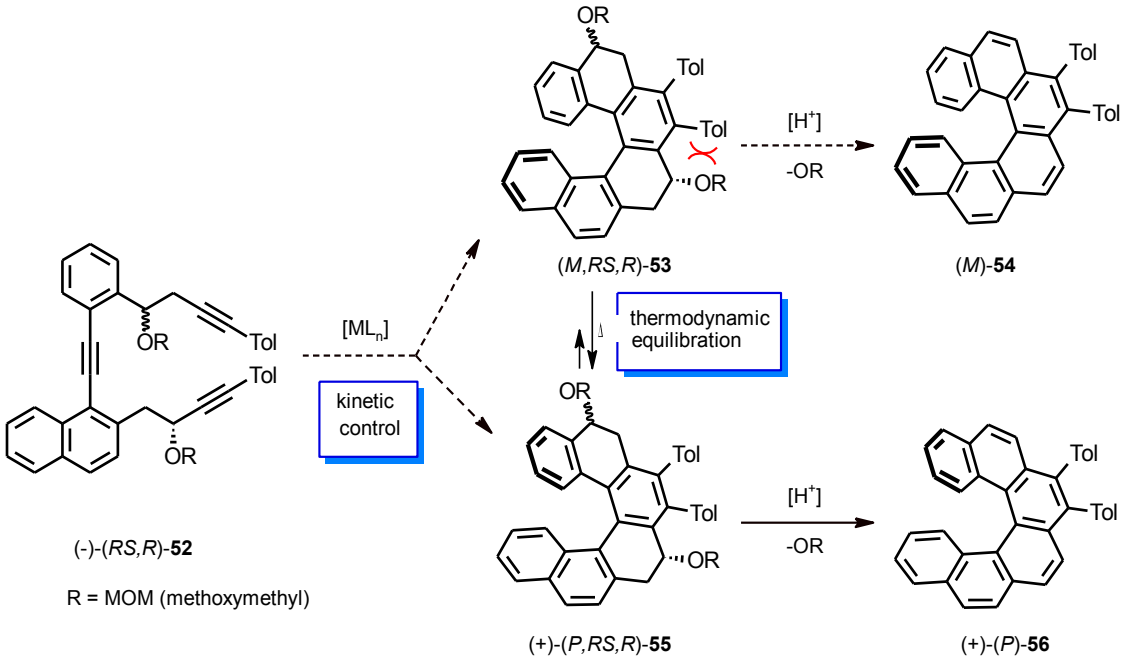
It was confirmed experimentally that diastereomers (*P,R,R*)- and (*M,R,R*)-**48** co-exist in a ratio of 66 : 34, whereas (–)-(*M,R,R*)-**49** prevails exclusively (>99 : <1 *dr*). The authors concluded that the stereochemical outcome of the cycloisomerisation is driven by an 1,3-allylic-type strain[61,62] between the methyl group at the chiral centre oriented in a pseudo-equatorial position and the tolyl group at the newly formed central benzene ring in (*P,R,R*)-**49**, the constellation the molecule wants to prevent (**Figure 2**). This thermodynamic stereocontrol operates in the post-cyclisation equilibration when helicity interconversion may occur, *i.e.* at high temperatures and at suitable helicene skeletons. This implies that such oxahelicenes can be utilised as a single-helicity chiral entities regardless of their barrier to helical epimerisation.

This methodology provides access to the optically pure oxa[5]-, oxa[6]- and oxa[7]helicenes bearing 2*H*-pyran rings in the scaffold. Additionally, it tolerates a large variety of substituents at the skeleton. Furthermore, this approach was used for the construction of the longest helicene ever synthesised (**Scheme 15**). Oxa[19]helicene (–)-(*M,R,R*)-**51** was synthesised by a quadruple Co^{I}-catalysed [2+2+2] cyclotrimerisation using a flow reactor. In a single transformation, twelve carbon-carbon bonds and twelve new rings were formed.[63]



Scheme 15 Diastereoselective synthesis of oxa[19]helicene **51**

Moreover, Stará and Starý *et al.* applied the same principle in the asymmetric synthesis of optically pure fully aromatic [5]-, [6]- and [7]helicenes.[64] The methodology described here takes advantage of a traceless chiral auxiliary, which is cleaved after the thermodynamic post-cyclisation equilibration (**Scheme 16**). Recently, enantiopure 2-amino [6]helicenes were also synthesised using the same concept.[65]

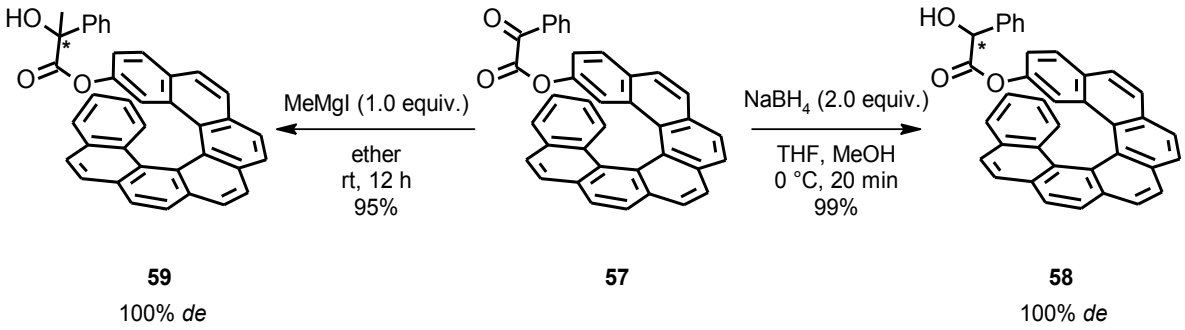


Scheme 16 Diastereoselective [2+2+2] cycloisomerisation towards carbohelicenes

1.2 APPLICATIONS OF HELICAL LIGANDS IN ASYMMETRIC CATALYSIS

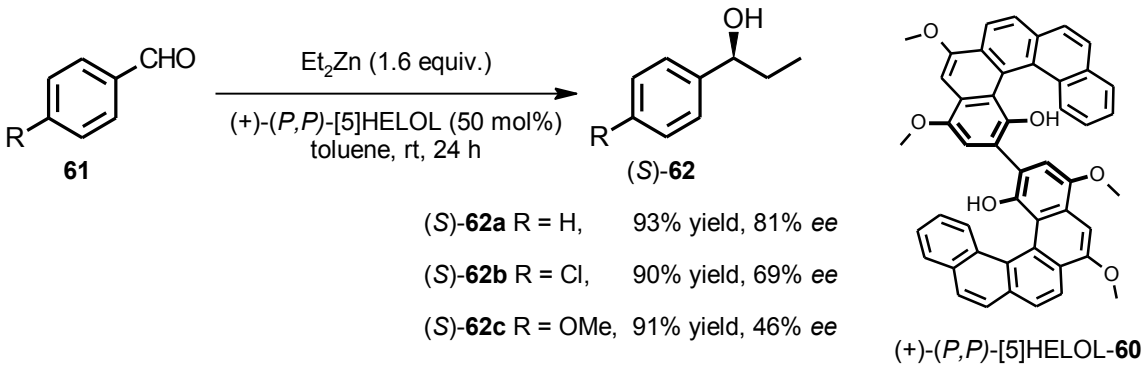
In the past, the lack of a general methodology for the preparation of optically pure helicenes and their derivatives limited their use as chiral inducers in asymmetric catalysis. Consequently, the use of helicenes or helicene-like molecules in asymmetric catalysis still remains underdeveloped compared to other types of chirality (central, axial, *etc.*).[66,67]

In the mid 80's, Martin *et al.* pioneered the asymmetric synthesis using helicenes as chiral auxiliaries.[68–72] They demonstrated that racemic [7]helicen-2-yl keto ester **57** can be diastereoselectively reduced by $NaBH_4$ yielding hydroxy ester **58** with 100% *de*.[68] The same authors studied also an addition of a Grignard reagent to compound **57** affording **59** in high yield and with complete diastereoselectivity (**Scheme 15**).[70]



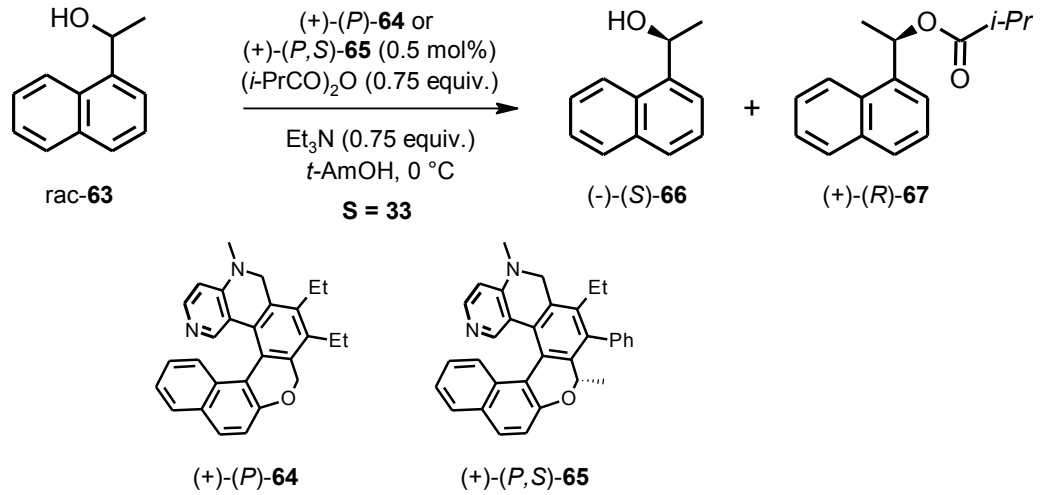
Scheme 15 Helicene as a chiral auxiliary in diastereoselective reduction of a C=O group and Grignard addition across the C=O group

Biaryl diols, like BINOL and VAPOL, are well known for their use in asymmetric catalysis.[73] Encouraged by the success of this type of ligands, Katz *et al.* synthesised the chiral bihelicenyl diol (+)-(*P,P*)-[5]HELOL **60** and studied the enantioselective addition of diethylzinc to benzaldehydes **61** to form alcohol **62**.[74] The [5]HELOL **60** provided *ee* of up to 81% (**Scheme 16**), which turned out to be superior to that of BINOL itself under the same reaction conditions.



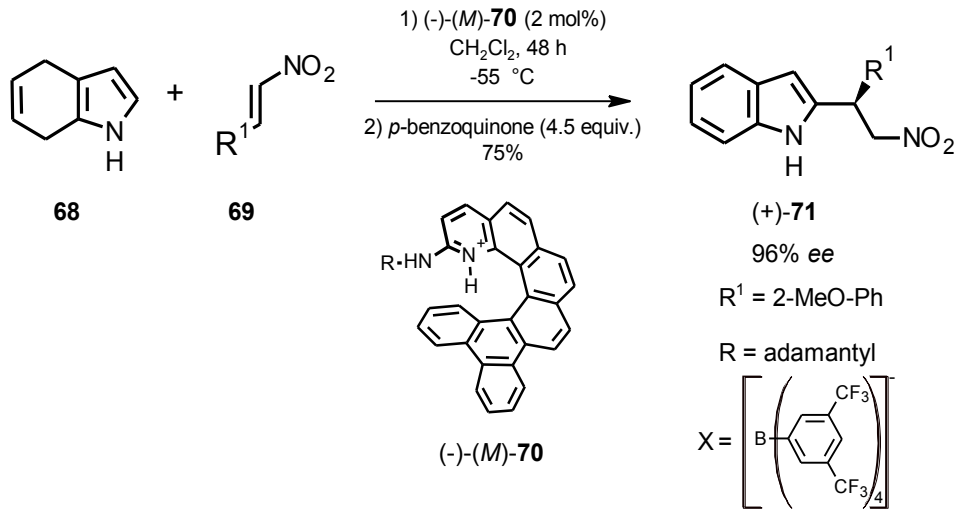
Scheme 16 Asymmetric diethylzinc addition to benzaldehyde promoted by [5]HELOL **60**

Stará and Starý *et al.* reported the first use of 1- and 2-aza[6]helicene in the kinetic resolution of racemic secondary alcohols.[75] While (+)-(*P*)-1-aza[6]helicene did not show any catalytic effect, (–)-(*M*)-2-aza[6]helicene promoted the acylation of *rac*-1-phenylethanol with isobutyric anhydride to yield (+)-(*R*)-1-phenylethanol in up to 99% *ee*. Later on, Carbery *et al*. introduced two helical analogues of 4-(dimethylamino)pyridine (DMAP), (+)-(*P*)-**64** and (+)-(*P,S*)-**65** as more efficient catalysts for similar transformation (**Scheme 17**).[76,77]



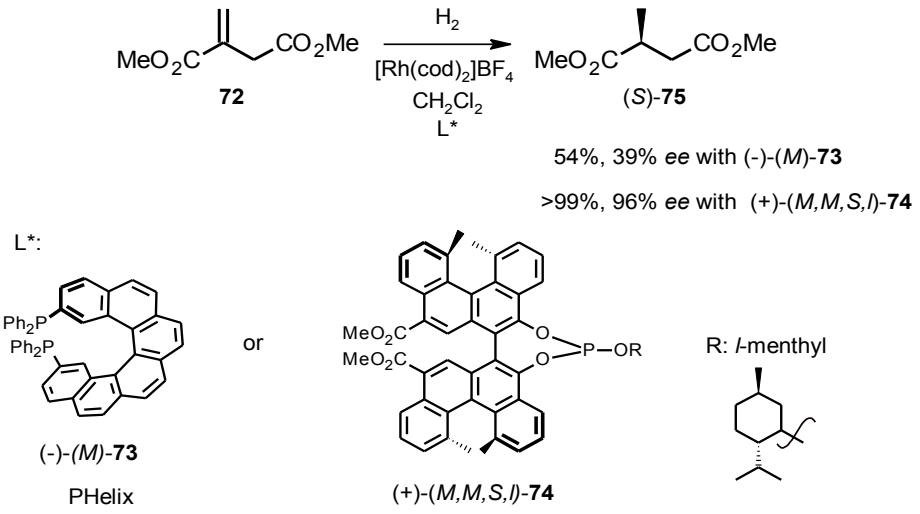
Scheme 17 Kinetic resolution of racemic secondary alcohols catalysed by the helical analogues of DMAP (+)-(*P*)-**64** and (+)-(*P,S*)-**65**

Takenaka and co-workers have also described several organocatalysts comprising a helicene unit in their scaffolds.[78] The helically chiral 2-aminopyridinium salts (–)-(*M*)-**70** and (+)-(*P*)-**70** were used as H-bonding donor in 1,4-addition of 4,7-dihydroindoles to olefins.[79] The substituted helically chiral 2-aminopyridinium salt (–)-(*M*)-**70** was used as catalyst under optimised conditions providing the product in moderated yield and with up to 96% *ee* (**Scheme 18**).



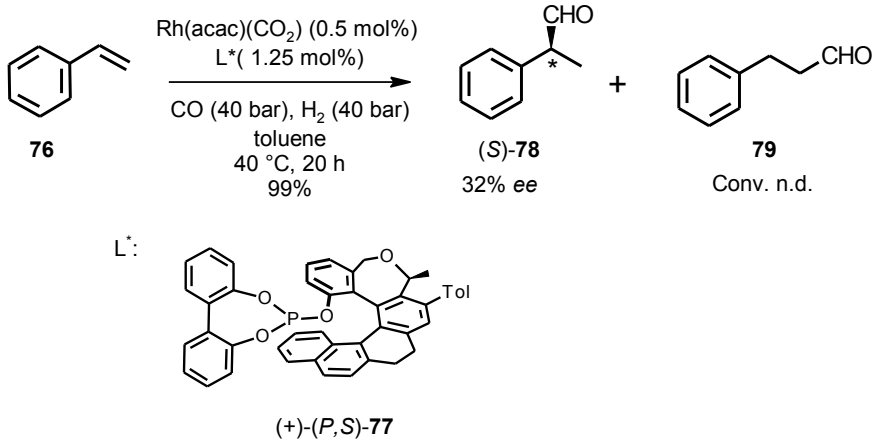
Scheme 18 Asymmetric 1,4-addition of 4,7-dihydroindoles to olefins catalysed by the helically chiral 2-aminopyridinium salt (–)-(*M*)-**70**

Not surprisingly, chiral helicene-based phosphorus ligands have attracted considerable attention.[1,8,9,11,80–83] Even though centrally, axially and planarly chiral phosphines have been extensively used in asymmetric catalysis in the past, it was not until 1997 when Reetz *et al.* described for the first time the use of the [6]helicene-derived diphosphine (–)-(*M*)-**73** (>98% *ee*) called PHelix. It was used in the rhodium catalysed hydrogenation of methyl itaconate **72** affording (*S*)-**75** with up to 39% *ee* (**Scheme 19**).[84] A few years later, Reetz and co-workers used the same diphosphine ligand in the palladium catalysed kinetic resolution of allylic esters.[85] Yamaguchi *et al*. was more successful in the rhodium catalysed hydrogenation of methyl itaconate **72** by applying four diastereoisomeric bishelicenol phosphites, which combine helical, axial and central chirality, and obtained the product (*S*)-**75** with high conversion and enantiomeric excess (**Scheme 19**), (up to 96% *ee* with (+)-(*M,M,S,l*)-**74**).[86]



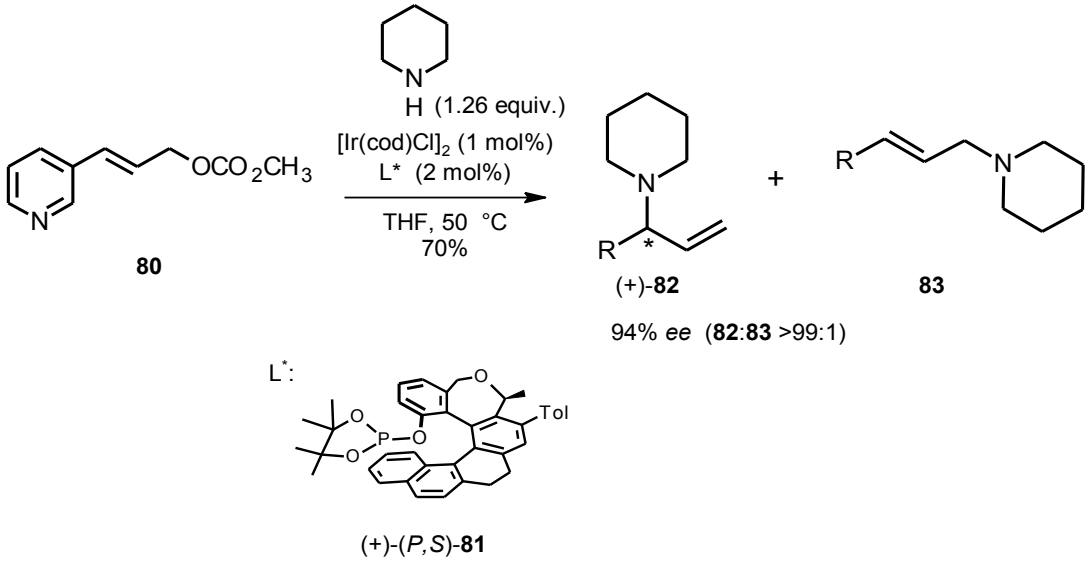
Scheme 19 Enantioselective rhodium catalysed hydrogenation of methyl itaconate **72**

Eilbracht, Stará and Starý *et al*. synthesised four new [6]helicene-like phosphites.[87] The helically chiral ligands like (+)-(*P,S*)-**77** and (+)-(*P,S*)-**81**, respectively, were applied in the Rh^{I}-catalysed hydroformylation of terminal alkenes (**Scheme 20**) and in the asymmetric Ir^{I}-catalysed allylic amination (**Scheme 21**). The hydroformylation led to the branched product (*S*)-**78** with high regioselectivity and conversion but provided only moderate enantiomeric excess of 32% *ee* at best.



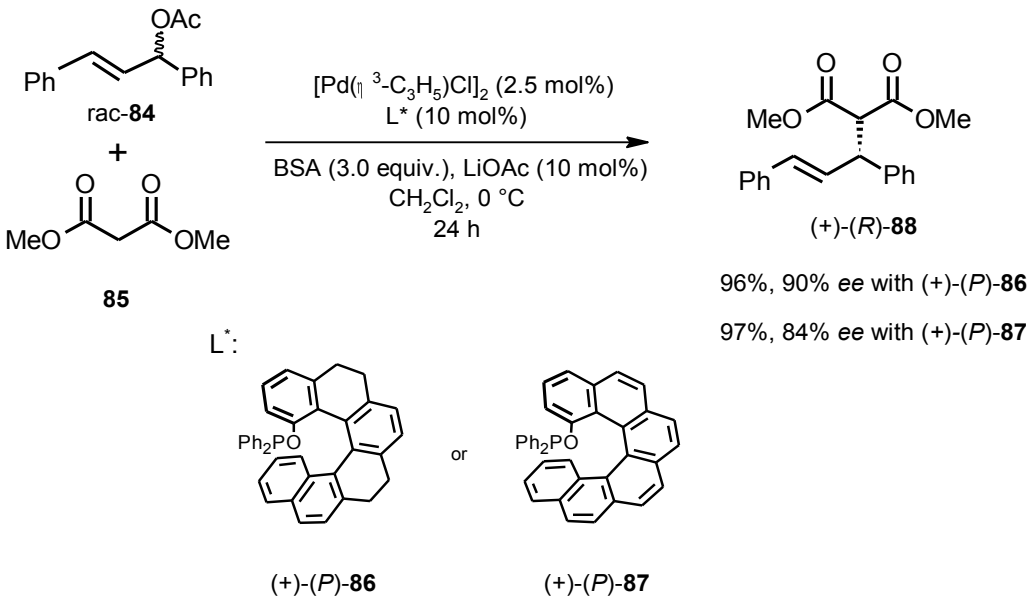
Scheme 20 Enantioselective Rh^{I}-catalysed hydroformylation of terminal alkenes

However, the ligand containing the pinacol fragment (+)-(*P,S*)-**81** was applied in the iridium catalysed asymmetric allylic amination of a cinnamyl-type substrate to exhibit high regioselectivity and enantioselectivity reaching up to 94% *ee* of (+)-**82**.



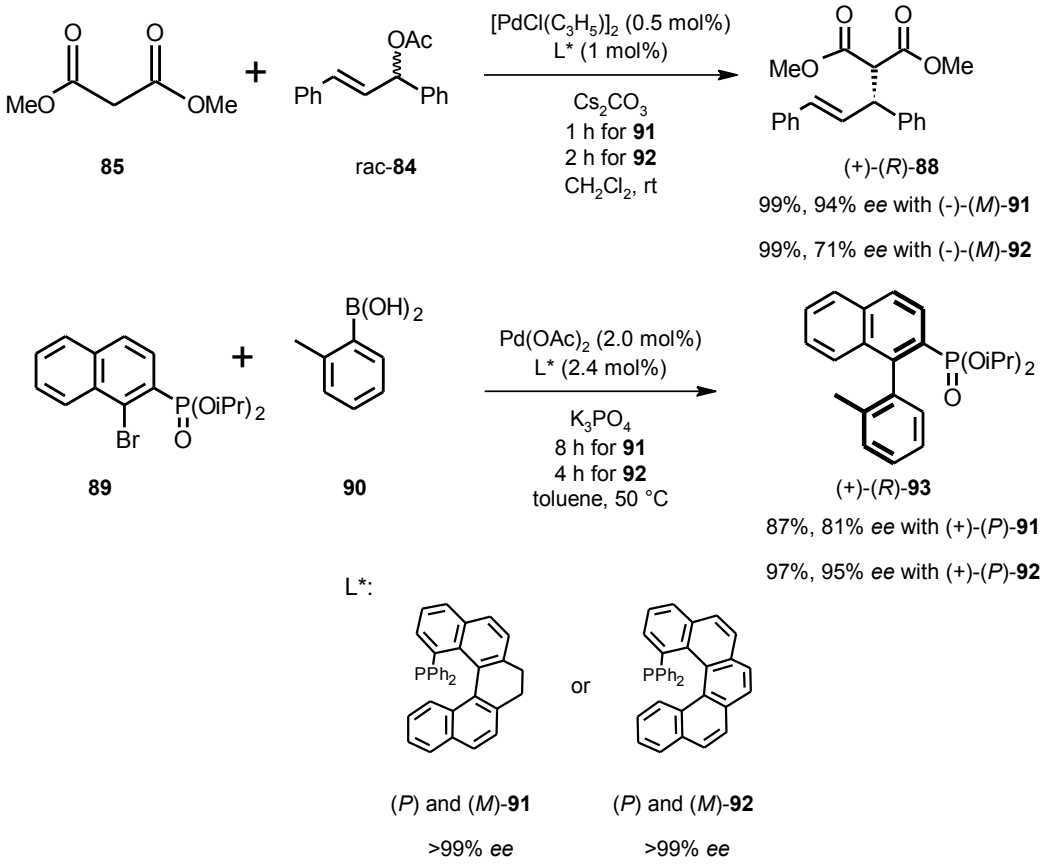
Scheme 21 Asymmetric iridium catalysed allylic amination of allyl carbonates

The availability of the optically pure helicenes in large-scale is crucial for their successful application in asymmetric catalysis. Recently, Tsujihara and Kawano *et al*. published a multigram-scale Ni^0-catalysed [2+2+2] cyclotrimerisation leading to racemic [6]helicen-1-ol derivatives.[88] (1*S*)-Camphanic chloride was then used as a derivatising reagent to resolve the diastereomeric mixture of camphanate esters by flash column chromatography and subsequent hydrolysis afforded enantiomerically pure [6]helicenols, which were then transformed into phosphinites (+)-(*P*)-**86** and (+)-(*P*)-**87** and used in the catalytic asymmetric allylic alkylation furnishing product (+)-(*R*)-**88** with up to 90% *ee* (**Scheme 22**).



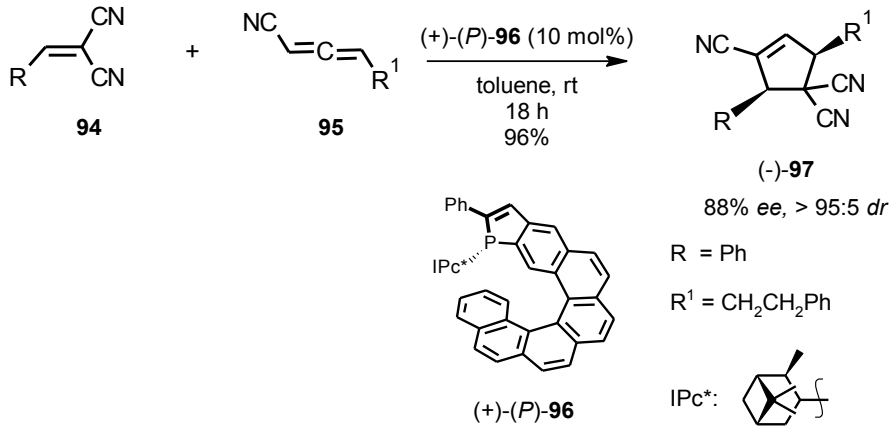
Scheme 22 Enantioselective palladium catalysed allylic alkylation

Suemune and Usui *et al*. succeeded in synthesising optically pure [5]helicenylphosphine ligands (+)-(*P*)-**91**, (–)-(*M*)-**91**, (+)-(*P*)-**92**, (–)-(*M*)-**92** that were applied in the Pd-catalysed asymmetric allylic substitution and Suzuki-Miyaura coupling.[22] Whereas the partially saturated phosphine (–)-(*M*)-**91** performed better in the first reaction (obtaining (+)-(*R*)-**88** with up to 94% *ee*), the fully aromatic (+)-(*P*)-**92** showed the more efficient axial-to-helical chirality transfer (obtaining (+)-(*R*)-**93** with up to 95% *ee*) in the palladium catalysed Suzuki-Miyaura coupling (**Scheme 23**).



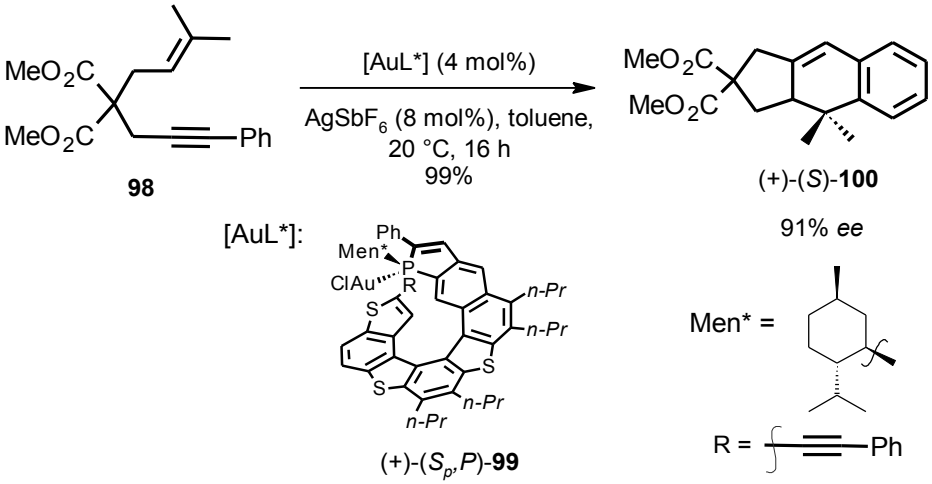
Scheme 23 Asymmetric palladium catalysed allylic substitution & Suzuki-Miyaura coupling

Apart from the aforementioned helicene-derived phosphines or phosphites, in which the phosphorus moiety is attached to the helicene scaffold, the phosphorus atom can also be embedded directly in to the helicene scaffold. Accordingly, the 1*H*-phosphole heterocycle can be located either in the centre[89,90] or at the end of the helicene skeleton. Marinetti *et al*. synthesised a series of phosphahelicene- and phosphathiahelicene-gold complexes bearing the phosphole unit at the end of the helicene scaffold.[91,92] They applied for the first time phosphahelicenes in the asymmetric catalytic [3+2] cyclisation of γ-substituted allenes and electron-poor olefins reaching up to 97% *ee* (**Scheme 24**).[93]



Scheme 24 Asymmetric catalytic [3+2] cyclisation of γ-substituted allenes and olefins

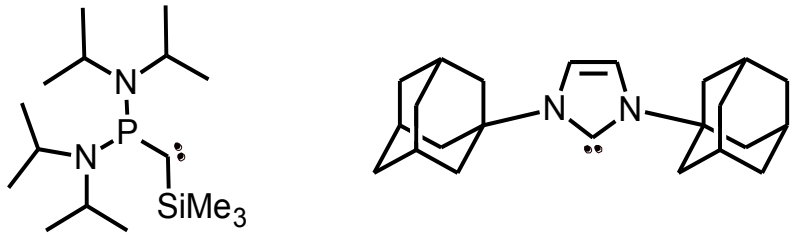
Marinetti and co-workers have broadened a portfolio of helicene-derived phosphole ligands (and their gold complexes) utilising a modular synthetic approach to this class of compounds. Such helically chiral gold catalysts were employed in the [4+2] cyclisation of 1,6-enynes. Dihydrocyclopenta[*b*]naphthalene (+)-(*S*)-**100** was obtained in 99% yield and with 91% *ee* when (+)-(S_p,*P*)-**99** was used (**Scheme 25**).[94]



Scheme 25 The use of helicene ligands in asymmetric [4+2] cycloaddition of 1,6-enyne

1.3 N-HETEROCYCLIC CARBENES

A neutral molecule that possesses a carbon with two unshared electrons and a six-electron valence shell fulfils the definition of carbene.[95] Although carbenes were postulated more than one hundred years ago,[96,97] it was not until recently that these highly reactive intermediates were isolated. In 1988, Bertrand *et al.* isolated for the first time a stable carbene (phosphinocarbene **101**), in which the geminal phosphorus and silicon substituents prevented its decomposition (**Figure 3**).[98] Despite the efforts of Wanzlick and Öfele [99–101] in the field of N-heterocyclic carbenes (NHCs), it was Arduengo *et al*. who isolated and characterised the first NHC, 1,3-bis(1-adamantyl)imidazol-2-ylidene (IAd) **102** (**Figure 3**), as a crystalline compound in 1991.[102] This discovery marked a paradigm shift in the field of carbene chemistry and, subsequently, NHCs have become an important class of compounds in contemporary chemistry.



101 IAd **102**

Figure 3 Bertrand's and Arduengo's isolated carbene **101** and NHC **102**, respectively

Carbenes can be either in a singlet or a triplet state. NHCs are usually singlet-ground-state type carbenes, where the carbene carbon is embedded into a heterocycle with at least one nitrogen atom in the ring (**Figure 4**). As an essential feature, the carbene carbon (C^2) has a vacant *p* orbital and an electron pair in an sp^2 hybridised orbital. The stability of the carbene is controlled by steric and electronic effects. In the case of IAd **102** it was shown that the adamantyl groups kinetically stabilise the carbene by preventing its dimerisation (known as Wanzlick equilibrium).[99,103] In addition to the steric effects, an electronic "push-pull effect"

of the neighbouring nitrogen atom(s) provides further important thermodynamic stabilisation. The "push-pull effect" comprises a simultaneous positive mesomeric effect (+M) and a negative inductive effect (-I). The electron density flows from the lone pair of a nitrogen/heteroatom towards the empty *p* orbital of the carbene carbon. At the same time, the electron density is decreased by the σ-electron-withdrawing nature of the nitrogen (**Figure 4**).[104]

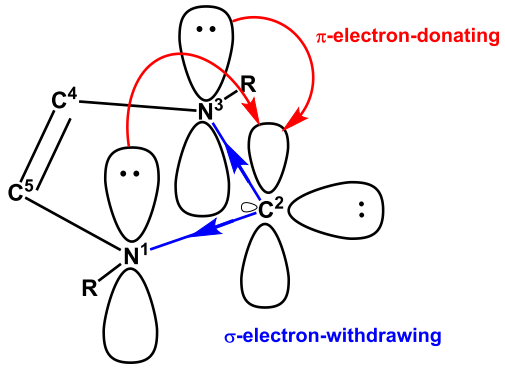


Figure 4 Ground-state electronic structure of imidazol-2-ylidenes

The relatively simple diversification of azolium precursors can expand the portfolio of NHC ligands that can be further studied. Therefore, a wide variety of structurally different NHCs and their complexes can be found in the literature.[105–107] The most common NHCs used in the field of organometallic chemistry and catalysis are based on imidazole (**103**, *e.g.* IMes), imidazoline (**104**, *e.g.* SIMes), oxazole (**105**), thiazole (**106**), triazole (**107**) and benzimidazole (**108**) (**Figure 5**). Recently, interest in so-called mesoionic or "abnormal" carbenes (**109**)[108] and cyclic (alkyl)(amino)carbenes (**110**), better known as (CAACs),[109] has been increasing.

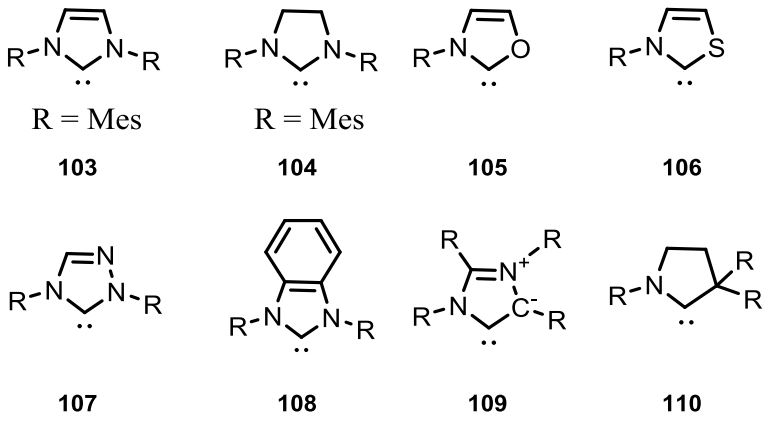
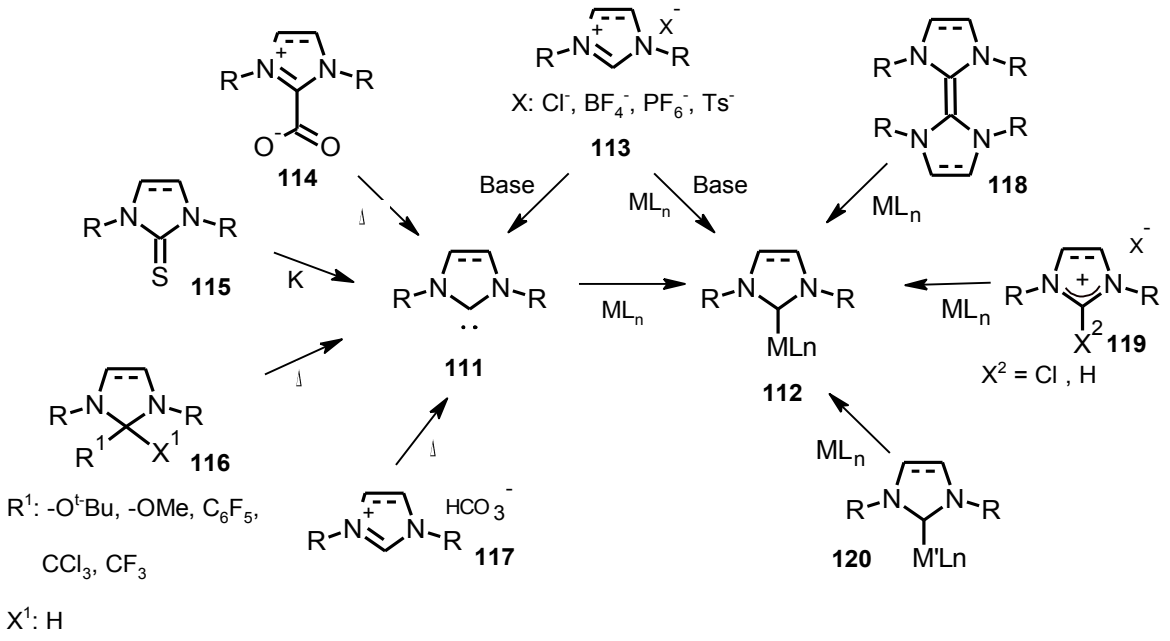


Figure 5 General structures of common NHC ligands

1.3.1 Synthesis of NHC and metal-NHC complexes

General synthetic routes towards NHC **111** and metal-NHC complexes **112** are presented in **Scheme 26**.[110] The synthetic scheme is mainly based on imidazol or imidazolium salts as precursors. Compound **111** can be generated from the corresponding imidazolium chlorides, tetrafluoroborates, hexafluorophosphates and tosylates **113** through deprotonation by a base.[111] Compound **114** is a carbene pre-trapped with carbon dioxide. It is air and moisture stable, easily isolated due to its insolubility in THF and it releases carbene **111** upon heating.[112] Thiones **115** are prepared from thioureas through condensation,[113] under acidic conditions from isothiocyanates,[114] also by reacting 1,2-diamines with thiophosgene[115] or by oxidation of the carbene with elemental sulphur.[116] In this case, carbene **111** is formed by reduction of thiones **115** using potassium.[113] Thermolysis of an alkoxy, pentafluoroaryl or haloformyl adduct **116** also affords carbene **111**.[117–119] Notably, bicarbonate **117** do not require the use of a base and produce carbene **111** upon thermolysis[120,121] (**Scheme 26**).



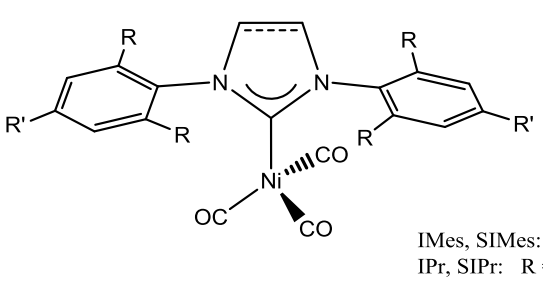
Scheme 26 Different routes towards free carbenes and metal-NHCs complexes

It should be emphasised that the azolium precursors are much more stable than the NHCs, which, though occasionally stable enough to be isolated, require handling in a glovebox or using the Schlenk techniques due to their air and moisture sensitivity. Upon coordination, the metal-NHC complexes are more stable than NHCs. The metal-NHC **112** can be obtained by a direct coordination of NHC **111** to metals.[122–124] Another approach is deprotonation of **113** in the presence of a transition metal.[100,101,125] Lappert *et al.* introduced a different approach that is based on the cleavage of electron-rich enetetramines **118** by transition metals.[126] Another method for the preparation of metal-NHC **112** is oxidative addition of a low valent metal complex to **119**.[127,128] The last example shows a popular and frequently used transmetallation of a pre-synthesised metal-NHC **120**, which is often a silver complex.[129]

1.3.1.1 Steric and electronic properties of NHC ligands

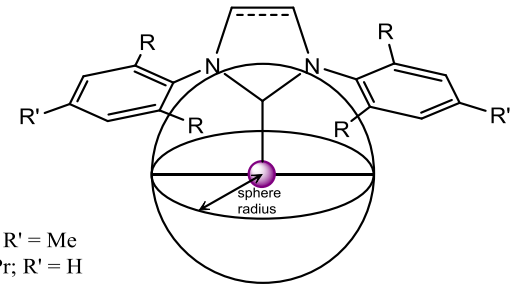
Like phosphines, NHCs can bind to metal centres forming metal complexes metal-NHC.[125] In contrast to phosphine ligands, their σ-donating properties are more pronounced resulting in a stronger metal-NHC bond. Additionally, their higher bond dissociation energies prevent a metal decomplexation.[130,131]

The steric and electronic properties of the NHC ligands are often characterised by the Tolman electronic parameter (TEP)[132,133] and the "percent buried volume (%V_{bur})".[134,135] While the first one describes the electronic effect of the ligand on the metal which is reflected in the stretching vibration frequency of the carbon monoxide ligands in the IR spectra,[136] the %V_{bur} expresses the portion of the volume of a sphere, which is centred on the metal, occupied by the NHC (**Figure 7**).



IMes, SIMes: R = R' = Me
IPr, SIPr: R = *i*-Pr; R' = H

121



122

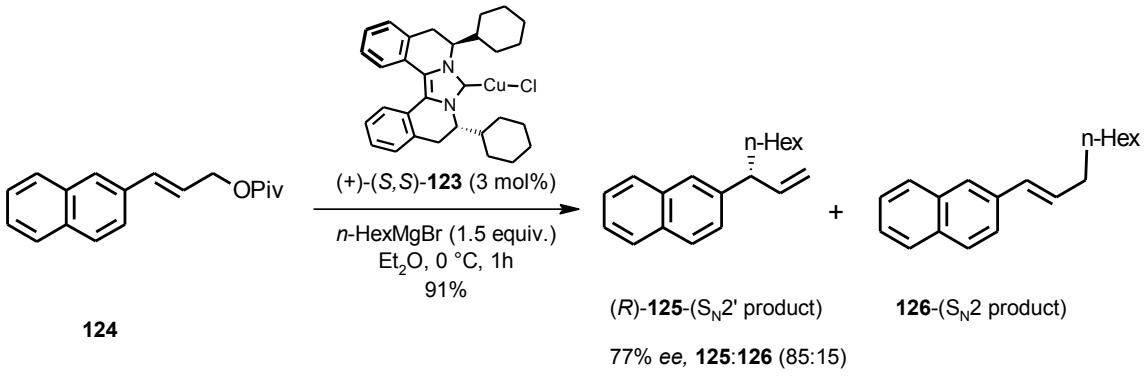
	121a	**121b**	**121c**	**121d**
$[Ni(CO)_3(NHC)]$	IMes	SIMes	IPr	SIPr
V_{CO} (CH_2Cl_2) cm^{-1}	2050.7	2051.5	2051.5	2052.2

	122a	**122b**	**122c**	**122d**
$[IrCl(CO)_2(NHC)]$	IMes	SIMes	IPr	SIPr
%V_{bur}	31.2	32.7	31.9	35.7

Figure 7 Tolman electronic parameter (TEP) for $Ni[(CO)_3(NHC)]$ and the representation of the sphere used to calculate the %V_{bur} for $[IrCl(CO)_2(NHC)]$

1.3.2 Helicene-based NHCs

Despite the vast number of chiral NHCs reported,[137,138] there are not many examples of helically chiral NHCs reported in the literature. Moreover, only a few of the existing examples have been used as chiral ligands in asymmetric catalysis. Hong *et al*. synthesised a biisoquinoline-based chiral diaminocarbene copper complex (+)-(*S,S*)-**123**[139] following Herrmann methodology.[140] Complex (+)-(*S,S*)-**123** was used in the enantioselective allylic alkylation with Grignard reagents reaching up to 77% *ee* and an 85:15 ratio of S_N2' *vs*. S_N2 (**Scheme 27**). Despite the helical chirality of the biisoquinoline-derived diaminocarbene unit in the metal-complex (+)-(*S,S*)-**123**, the authors did not study its conformational stability or the role in the chirality transfer.[139]



Scheme 27 Helical NHC Cu complex in enantioselective S_N2' allylic alkylation

Crassous *et al*. prepared the first enantiopure helicene-NHC-iridium complexes (+)-(*P,S*$_{Ir}$)-**127** and (–)-(*M,R*$_{Ir}$)-**127** utilising a racemate resolution by HPLC on a chiral column (**Figure 8**).[141] The authors stated that potential applications of (+)-(*P,S*$_{Ir}$)-**127** and (–)-(*M,R*$_{Ir}$)-**127** in asymmetric catalysis were under investigation. In 2017, Crassous *et al.* constructed (+)-(*P*,Λ_{Ir})-**128**, which exhibited a very long-lived circularly polarised (CP) blue-green phosphorescence (**Figure 8**).[142] In this case, the helical iridium complex may have potential application as chiral dopant in circularly polarised organic light-emitting diodes CP-OLEDs[143] or singlet-oxygen sensitisers.[144]

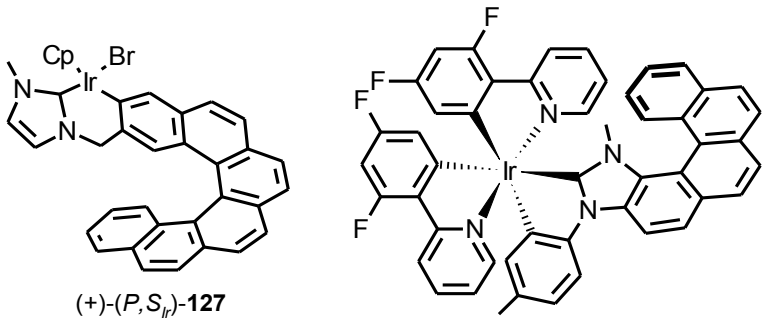
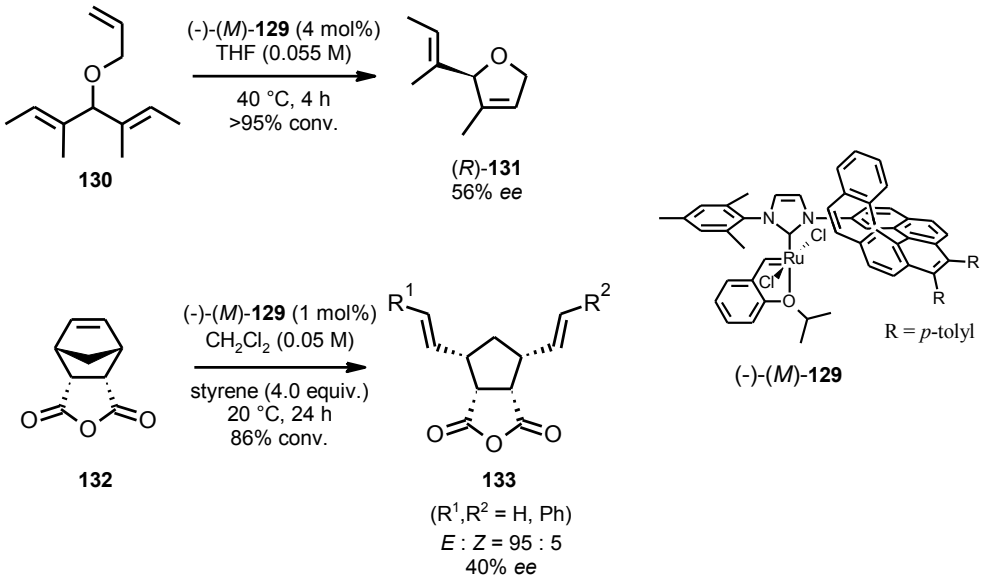


Figure 8 Helically chiral iridium-NHC complexes

Another example of optically pure helical NHC was published recently by Stará, Starý and Schmidt *et al.*[145] The authors described the formation of the first helically chiral ruthenium complex (–)-(*M*)-**129** and its application in the asymmetric ring closing metathesis (RCM) and ring opening metathesis - cross metathesis (ROM-CM) (**Scheme 28**). The study presented good conversion, good regioselectivity and moderate enantioselectivity.



Scheme 28 RCM and ROM-CM catalysed by a helical ruthenium complex

2 AIM & OBJECTIVES

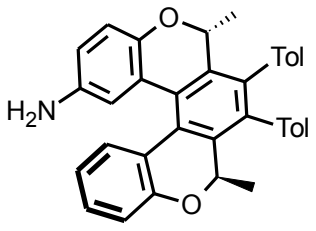
2.1 AIM

The difficulty of synthesising nonracemic helicenes was emphasised in the Introduction Chapter along with the fact that it has limited their use as chiral ligands in asymmetric catalysis. Compared to axially, centrally and planarly chiral ligands, the helically chiral ones thus remain rather unexplored. The few examples of asymmetric catalysis presented in the literature so far utilised mainly helically chiral phosphine ligands. Despite their superior catalytic feature, helicene-based N-heterocyclic carbenes that can serve as chiral ligands have so far been scarce in the literature. *The aim of my Thesis was to synthesise optically pure helically chiral imidazolium salts as precursors of NHCs and apply them to asymmetric catalysis.*

The imidazolium core unit was selected preferentially over other heterocycles because of its direct synthetic accessibility as compared to other NHC precursors (**Figure 5**). For the synthesis of helicenes that are connected to the imidazolium core, I proposed to take advantage of the well-established modular methodology for the preparation of diastereo- and enantiopure oxa[5]-, oxa[6]- and oxa[7]helicenes bearing 2*H*-pyran rings in the scaffold.[60] Furthermore, such an approach would allow for an efficient modification of the oxahelicene backbone that should enable a study on the ligand structure-reaction enantioselectivity relationship. Accordingly, I decided to synthesise diastereo- and enantiopure building blocks derived from both oxa[5]- and oxa[6]helicene and to attach one or two such helical units to the NHC imidazolium precursor. Therefore, eight specific objectives have been defined in order to achieve the objective of my project.

2.2 OBJECTIVES

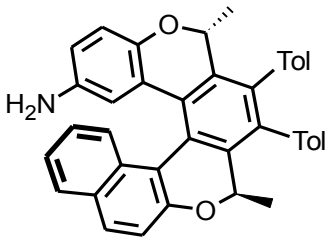
- The first objective was synthesis of diastereo- and enantiopure 2-aminooxa[5]helicene (*M,R,R*)-**134** as the main building block for the preparation of the respective symmetrical and unsymmetrical [5]helicene imidazolium salts (**Figure 9**).



(*M,R,R*)-**134**

Figure 9

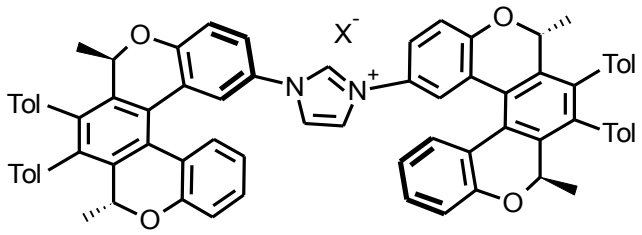
- The second objective was synthesis of diastereo- and enantiopure 2-aminooxa[6]helicene (*M,R,R*)-**135** as the main building block for the preparation of the respective symmetrical and unsymmetrical [6]helicene imidazolium salts (**Figure 10**).



(*M,R,R*)-**135**

Figure 10

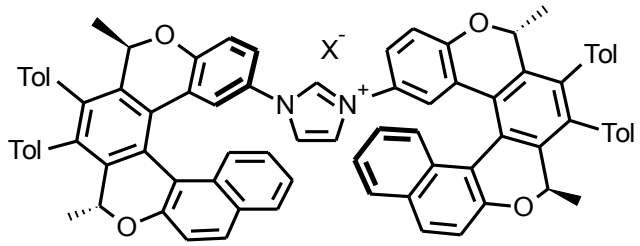
- The third objective was synthesis of the diastereo- and enantiopure symmetrical bis(oxa[5]helicenyl) imidazolium salt (*M,R,R*),(*M,R,R*)-**136** (**Figure 11**).



(*M*,*R*,*R*),(*M*,*R*,*R*)-**136**

Figure 11

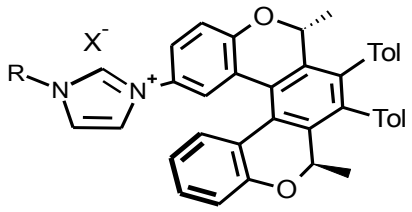
- The fourth objective was the synthesis of the diastereo- and enantiopure symmetrical bis(oxa[6]helicenyl) imidazolium salt (*M,R,R*),(*M,R,R*)-**137** (**Figure 12**).



(*M*,*R*,*R*),(*M*,*R*,*R*)-**137**

Figure 12

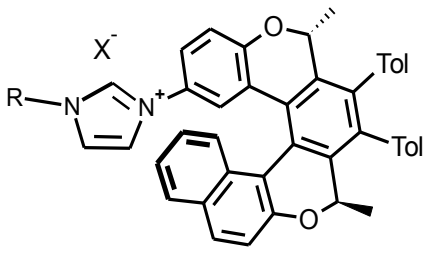
- The fifth objective was synthesis of the diastereo- and enantiopure unsymmetrical mono(oxa[5]helicenyl) imidazolium salt (*M,R,R*)-**138** (**Figure 13**).



(*M*,*R*,*R*)-**138**

Figure 13

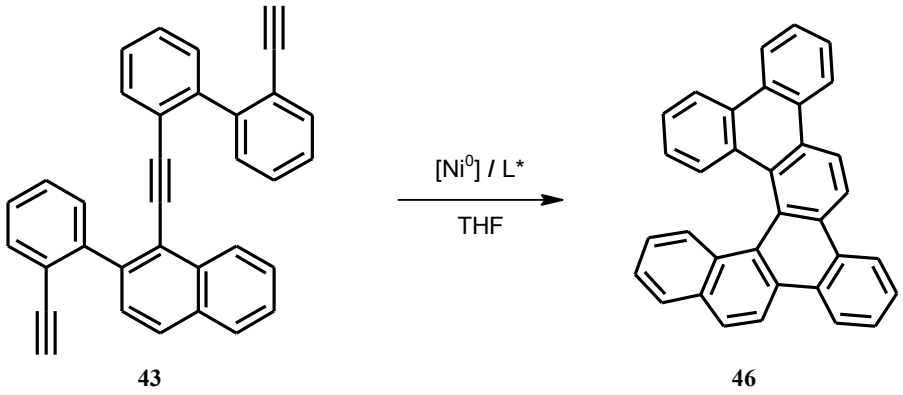
- The sixth objective was synthesis of the diastereo- and enantiopure unsymmetrical mono(oxa[6]helicenyl) imidazolium salt (*M,R,R*)-**139** (**Figure 14**).



(*M*,*R*,*R*)-**139**

Figure 14

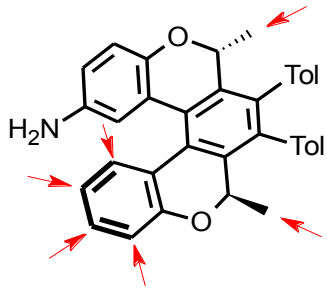
- The seventh objective was to apply the new helically chiral imidazolium salts **136**–**139** as NHC ligand precursors in Ni^0-catalysed [2+2+2] cycloisomerisation of tryine **43** leading to the nonracemic dibenzo[6]helicene **46** (**Figure 15**).



43 **46**

Figure 15

- The eighth objective was to synthesise a small portfolio of various diastereo- and enantiopure oxa[5]helicene-derived NHC precursors and to study the influence of the structural modifications of the respective NHC ligands on the chirality transfer in Ni^0-catalysed [2+2+2] cycloisomerisation of tryines to nonracemic dibenzohelicenes. The arrows point towards possible positions where the helical structure could be easily modified (*M*,*R*,*R*)-**140** (**Figure 16**).



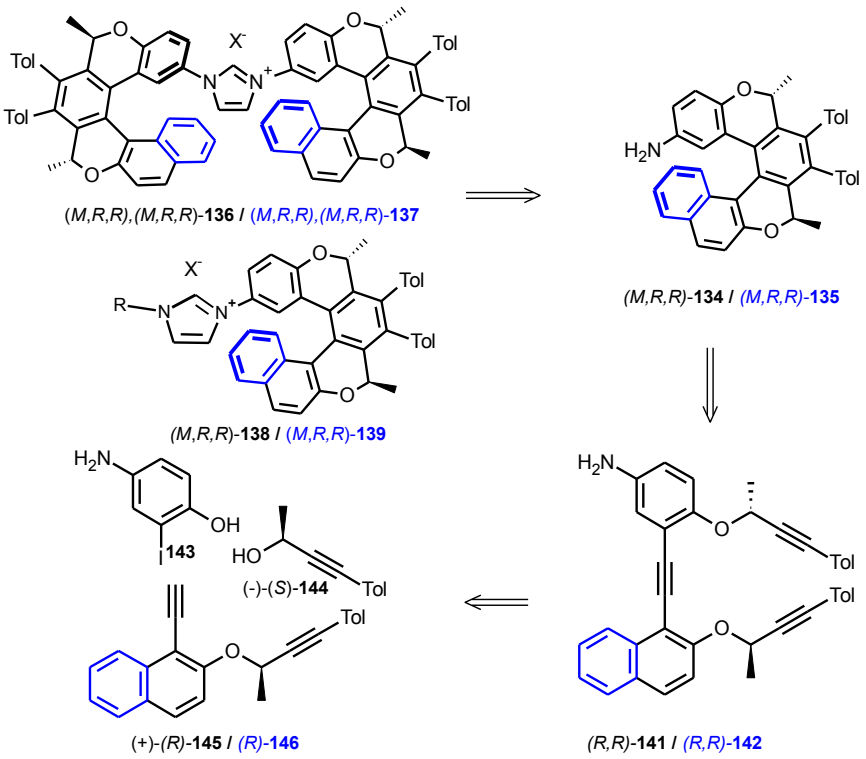
(*M*,*R*,*R*)-**140**

Figure 16

3 RESULTS & DISCUSSION

3.1 SYNTHESIS OF HELICENE BASED NHC LIGANDS

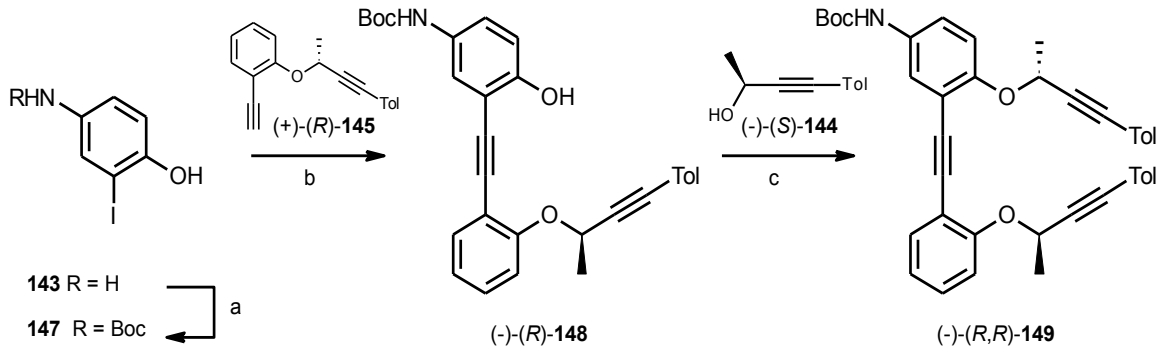
Retrosynthetic analysis of the target helically chiral imidazolium salts (*M,R,R*),(*M,R,R*)-**136**, (*M,R,R*),(*M,R,R*)-**137**, (*M,R,R*)-**138** and (*M,R,R*)-**139** indicated 2-aminooxahelicenes (*M,R,R*)-**134** and (*M,R,R*)-**135**, respectively, as the key building blocks (**Scheme 29**). These can be easily synthesised from the centrally chiral triynes (*R,R*)-**141** and (*R,R*)-**142**, respectively, using intramolecular metal catalysed [2+2+2] cyclotrimerisation. Triynes (*R,R*)-**141** and (*R,R*)-**142** can be prepared following a sequence of Sonogashira and Mitsunobu reactions from the different building blocks **143**, (–)-(*S*)-**144**[146], (+)-(*R*)-**145**[60] and (*R*)-**146** (**Scheme 29**).



Scheme 29 Retrosynthetic analysis of (*M,R,R*),(*M,R,R*)-**136**, (*M,R,R*),(*M,R,R*)-**137**, (*M,R,R*)-**138** and (*M,R,R*)-**139**. The blue ring corresponds to the extension of the structures by one ring.

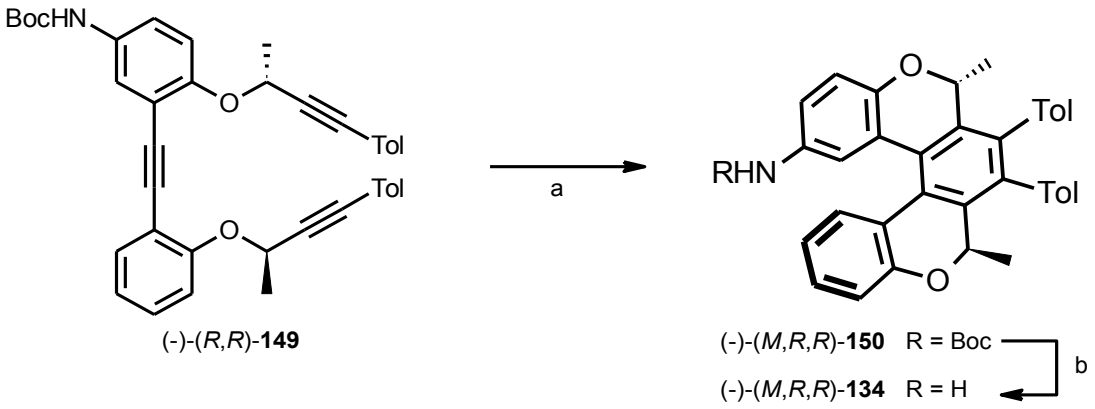
3.1.1 Synthesis of 2-aminooxa[5]helicene and 2-aminooxa[6]helicene

In order to avoid side reactions during the synthesis, the amino group of the key triyne (*R,R*)-**141** (**Scheme 29**) should stay protected by a suitable protecting group such as a *tert*-butyloxycarbonyl one (Boc) during its synthesis (–)-(*R,R*)-**149** (**Scheme 30**) (until a free amine would be liberated to synthesise the corresponding imidazolium salts). To this end, carbamate **147** was coupled with diyne (+)-(*R*)-**145** under Sonogashira reaction conditions to afford the hydroxy compound (–)-(*R*)-**148**. Mitsunobu reaction with the chiral alcohol (–)-(S)-**144** provided the key triyne (–)-(*R,R*)-**149**. Alcohol (–)-(*S*)-**144** was synthesised in one step from commercial (+)-(*S*)-3-butyn-2-ol and 4-iodotoluene by Sonogashira coupling reaction.[146] It is worth mentioning that both enantiomers of 3-butyn-2-ol are commercially available.



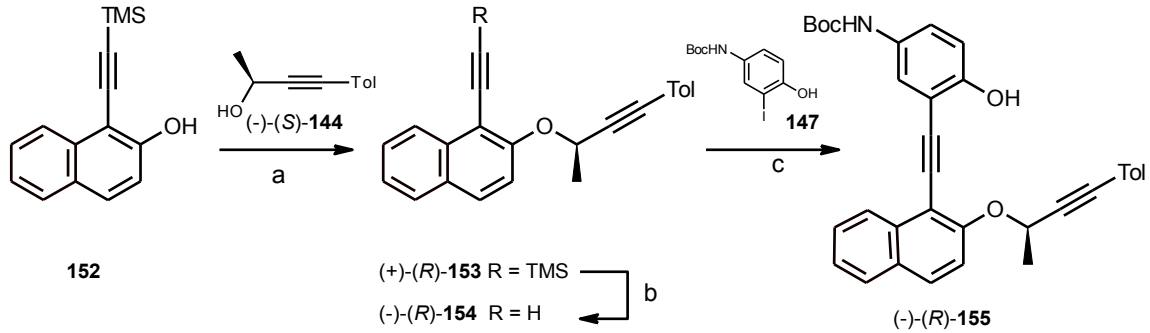
Scheme 30 (a) Boc_2O (1.1 equiv.), Et_3N (2.0 equiv.), MeOH, rt, 3 h, 96%; (b) (+)-(*R*)-**145** (1.3 equiv.), $PdCl_2(PPh_3)_2$ (2 mol%), CuI (4 mol%), *i*-Pr_2NH (2.0 equiv.), toluene, rt, 3 h, 85%; (c) (–)-(*S*)-**144** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 4 h, 90%.

The centrally chiral triyne (–)-(*R,R*)-**149** was then submitted to the metal catalysed [2+2+2] cyclotrimerisation using CpCo(CO)(fum)[147] as a catalyst. The reaction was successfully performed under microwave irradiation and the Boc-protected 2-aminooxa[5]helicene (–)-(*M,R,R*)-**150** was obtained in good yield. Finally, the protecting group was removed by trifluoroacetic acid providing the diastereo- and enantiopure 2-aminooxa[5]helicene (–)-(*M,R,R*)-**134** (**Scheme 31**).



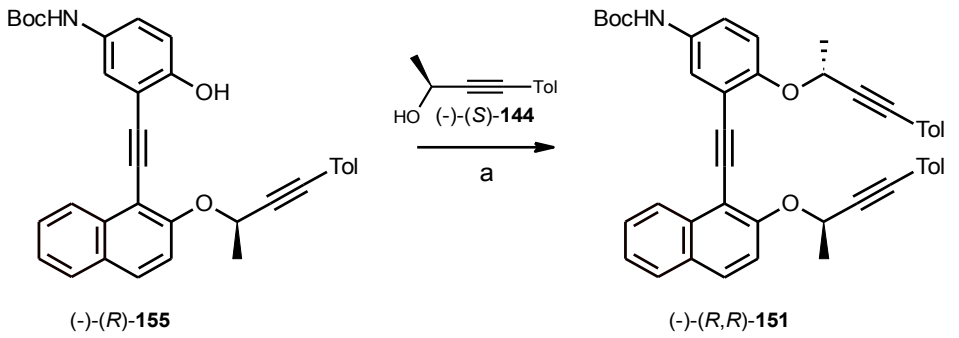
Scheme 31 (a) CpCo(CO)(fum) (30 mol%), μW, THF, [bdmim]BF_4, 140 °C, 15 min, 82%; (b) TFA (15 equiv.), CH_2Cl_2, rt, 16 h, 78%.

A similar synthetic route was used to synthesise the key triyne (–)-(*R,R*)-**151** (**Scheme 33**), a precursor to 2-aminooxa[6]helicene (–)-(*M,R,R*)-**135** (**Scheme 34**). First, compound **152** was synthesised according to the literature[76] from the commercially available 1-iodo-2-naphthol. The free alcohol **152** was reacted with (–)-(*S*)-4-(*p*-tolyl)but-3-yn-2-ol **144** under Mitsunobu reaction conditions providing the protected diyne (+)-(*R*)-**153** in high yield. After removal of the silyl protecting group, diyne (–)-(*R*)-**154** was submitted to Sonogashira reaction with *tert*-butyl (4-hydroxy-3-iodophenyl)carbamate **147** (**Scheme 32**).



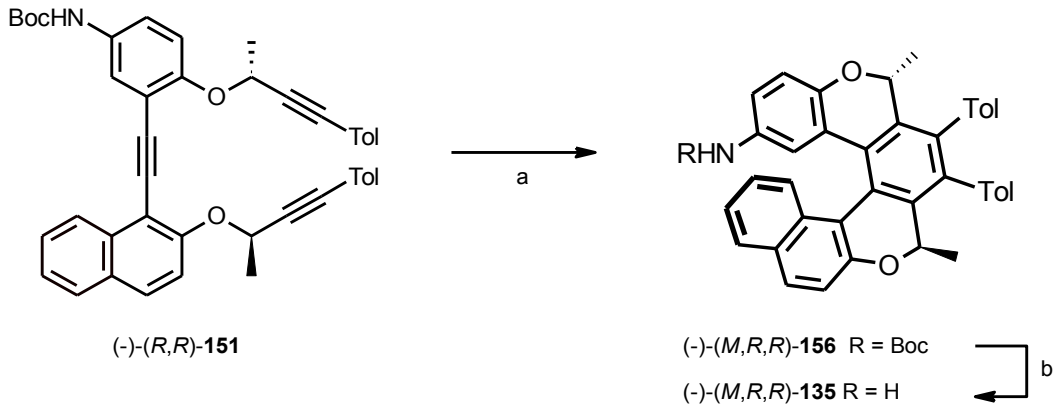
Scheme 32 (a) (–)-(*S*)-**144** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 2.5 h, 92%; (b) K_2CO_3 (2.0 equiv.), MeOH, rt, 3 h, 98%; (c) (–)-(*R*)-**154** (1.2 equiv.), $PdCl_2(PPh_3)_2$ (2 mol%), CuI (5 mol%), *i*-Pr_2NH (2.0 equiv.), benzene, 45 °C, 4.5 h, 83%.

The resulting alcohol (–)-(*R,R*)-**155** underwent another Mitsunobu reaction to afford the optically pure triyne (–)-(*R,R*)-**151** (**Scheme 33**).



Scheme 33 (a) (–)-(*S*)-**144** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 2.5 h, 88%.

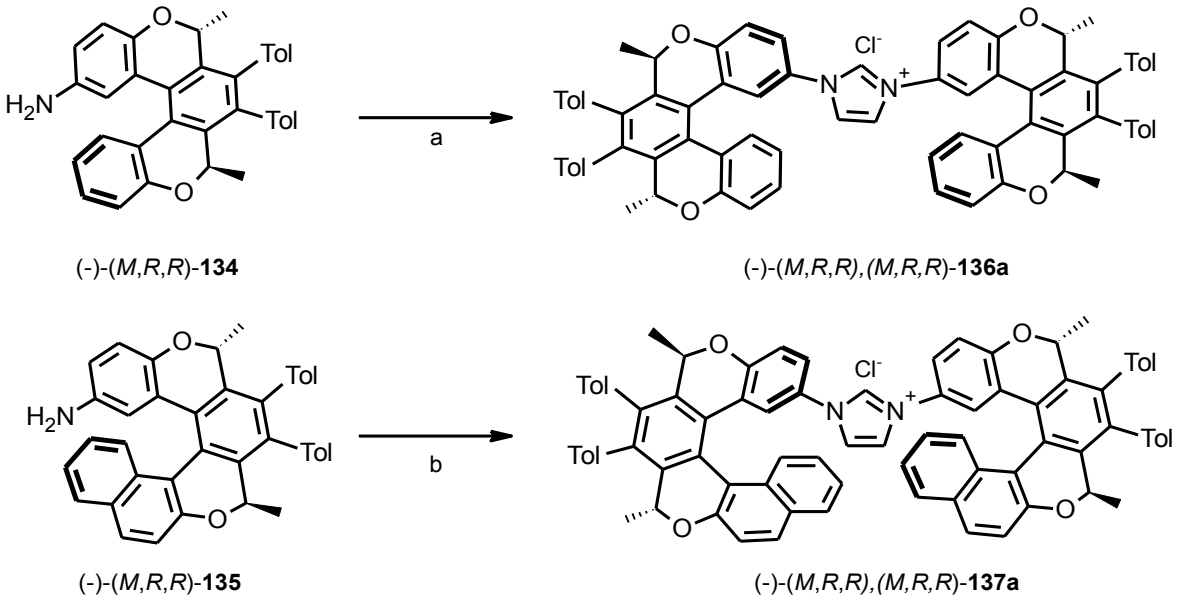
Triyne (–)-(*R,R*)-**151** was then submitted to the Co^I-catalysed [2+2+2] cyclotrimerisation under microwave irradiation, in which the desired Boc-protected aminooxa[6]helicene (–)-(*M,R,R*)-**156** was formed in moderate yield. Finally, the Boc protecting group was easily removed by trifluoroacetic acid providing the diastereo- and enantiopure 2-aminooxa[6]helicene (–)-(*M,R,R*)-**135** in good yield (**Scheme 34**).



Scheme 34 (a) CpCo(CO)(fum) (40 mol%), μW, THF, [bdmim]BF_4, 140 °C, 15 min, 63%; (b) TFA (15.0 equiv.), CH_2Cl_2, 16 h, rt, 77%.

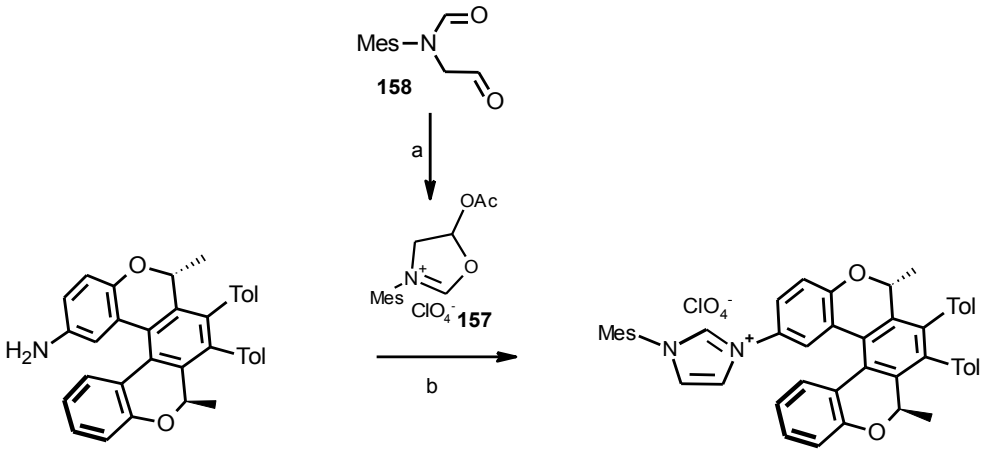
3.1.2 Synthesis of helically chiral imidazolium salts

A one pot procedure based on an acid-catalysed condensation of glyoxal, formaldehyde and primary amines,[148] which proceeds through a series of equilibrium steps to yield imidazolium salts,[149] was chosen for the synthesis of symmetrical 1,3-disubstituted helically chiral imidazolium salts. Thus, two equivalents of the primary amine, 2-aminooxa[5]helicene (–)-(*M,R,R*)-**134** or 2-aminooxa[6]helicene (–)-(*M,R,R*)-**135** were reacted with one equivalent of glyoxal and one equivalent of formaldehyde under mild conditions[150] to afford the desired symmetrical diastereo- and enantiopure bis(oxahelicenyl) NHC precursors (–)-(*M,R,R*),(*M,R,R*)-**136a** and (–)-(*M,R,R*),(*M,R,R*)-**137a** in good yields (**Scheme 35**).

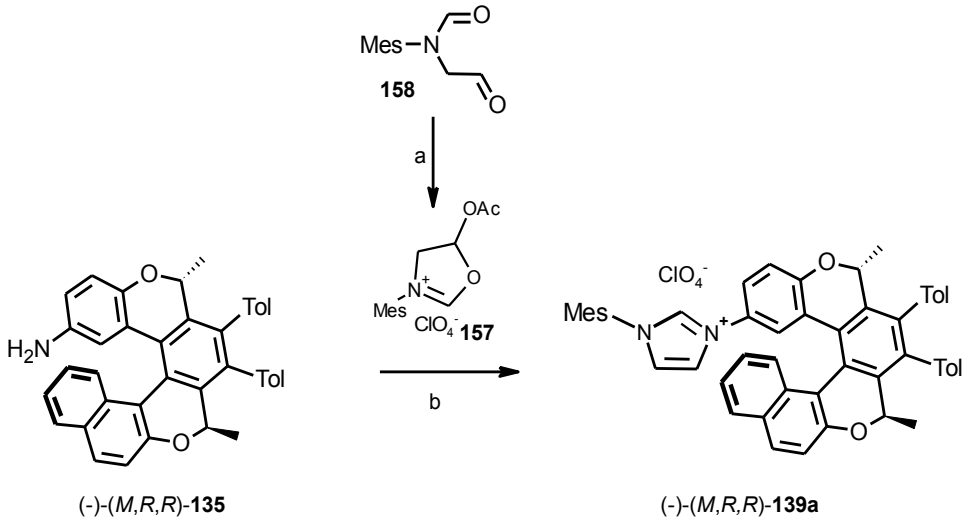


Scheme 35 (a) (–)-(*M,R,R*)-**134**, aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.7 equiv.), AcOH, 40 °C, 25 min, 66%; (b) (–)-(*M,R,R*)-**135**, aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.6 equiv.), AcOH, 55 °C, 35 min, 78%.

A stepwise procedure developed by Fürstner *et al.* was used for the synthesis of unsymmetrical 1-mesityl-3-(oxahelicenyl)imidazolium perchlorates (–)-(*M,R,R*)-**138a** and (–)-(*M,R,R*)-**139a**.[151] The oxazolium salt **157** (generated from the *N*-(2-oxoethyl)formamide derivative **158**) was reacted with 2-aminooxa[5]helicene (–)-(*M,R,R*)-**134** or 2-aminooxa[6]helicene (–)-(*M,R,R*)-**135** to give the unsymmetrical diastereo- and enantiopure salts (–)-(*M,R,R*)-**138a** and (–)-(*M,R,R*)-**139a** in acceptable yields and, therefore, the reaction conditions were not further optimised (**Scheme 36 and 37**).



Scheme 36 (a) **158** (1.9 equiv.), $HClO_4$ (3.6 equiv.), acetic acid anhydride, rt, 16 h; (b) toluene, rt, 4 h, then $HClO_4$ (3.6 equiv.), 80 °C, 16 h, 38%.



Scheme 37 (b) **158** (2.1 equiv.), $HClO_4$ (2.2 equiv.), acetic acid anhydride, rt, 16 h; (b) toluene, rt, 4 h, then $HClO_4$ (2.2 equiv.), 80 °C, 16 h, 28%.

3.2 APPLICATION OF SYMMETRICAL AND UNSYMMETRICAL IMIDAZOLIUM SALTS IN THE Ni^0-CATALYSED [2+2+2] CYCLOISOMERISATION

Metal catalysed intra- and intermolecular [2+2+2] cycloisomerisation of π-electron systems is an important method for the construction of carbo- and heterocycles.[152–154] In our group, this robust methodology has been established as an essential tool for the synthesis of helicenes. An enantioselective [2+2+2] cycloisomerisation is an atom-economic process that can deliver nonracemic helicenes. Therefore, the diastereo- and enantiopure mono- and bis(oxahelicenyl) salts (–)-(*M,R,R*)-**138a**, (–)-(*M,R,R*)-**139a**, (–)-(*M,R,R),(M,R,R*)-**136a** and (–)-(*M,R,R),(M,R,R*)-**137a** were utilised as stable precursors of helically chiral NHC ligands in the Ni^0-catalysed [2+2+2] cycloisomerisation of triyne **43** (prepared previously in our laboratory)[58] leading to the nonracemic dibenzo[6]helicene **46** (**Scheme 14**).

3.2.1 Enantioselective catalysis in the synthesis of nonracemic dibenzo[6]helicene

The nickel N-heterocyclic carbene complexes (Ni^0-NHC) are usually obtained by a direct substitution of labile ligands coordinated to Ni^0 in complexes such as $Ni(cod)_2$ or $Ni(CO)_4$ (the latter used less often due to its toxicity)[136] with a free carbene. Alternatively, Ni^0-NHC complexes can be conveniently generated by reduction of the more stable Ni^{II}-NHC complexes.[155] In addition to the direct ligand exchange,[156] these complexes can be prepared by transmetallation from a readily accessible silver carbene complex.[157]

Depending on the structure of the N-heterocyclic carbene(s) coordinated to the metal, a variety of Ni^0-NHC arrangements are possible,[158] both homoleptic and heteroleptic complexes with either two, three or four NHCs,[159,160] adopting various geometries (*e.g.* linear, planar or tetrahedral). Interestingly, most of the Ni^0 complexes bearing sterically demanding NHCs (such as IMes or IPr) are 14 electron compounds with linear geometry.[161,162] Unfortunately, attempts to isolate and characterise Ni complexes bearing the prepared helically chiral NHC ligands failed. Yet, based on analogy with the structures of other Ni^0-NHC complexes found in the Cambridge Structural Database (CSD) and further

supported by molecular modelling at the DFT level of theory, we propose that our helically chiral NHCs also form homoleptic 14 electron complexes with a linear geometry such as **159** (**Figure 17**).

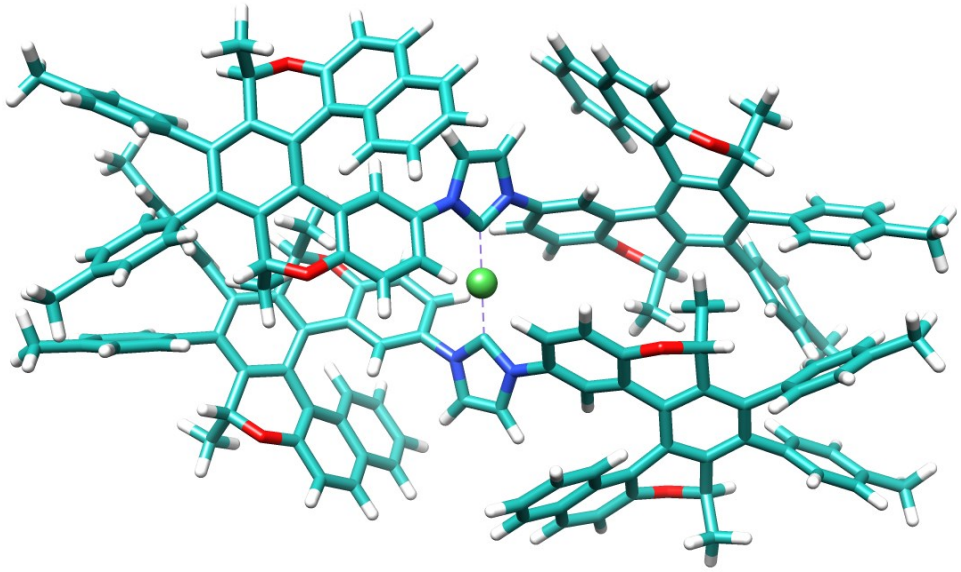
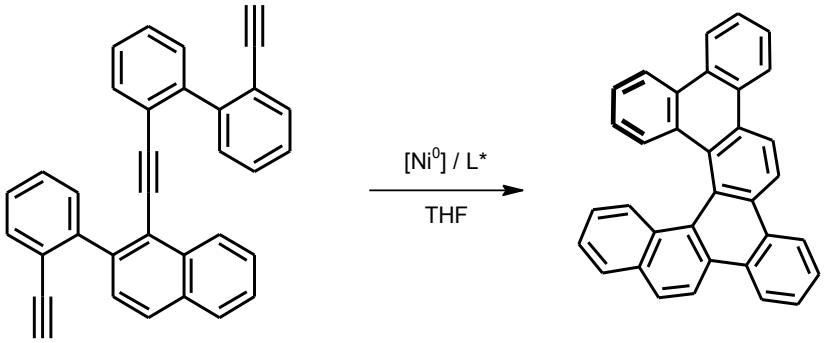


Figure 17 Graphic representation of the structure of the Ni^0-NHC complex **159** optimised at the RI-DFT (PBE0/def2-TZVP/GD3) level of theory using the Turbomole 7.1 program package (two NHC ligands generated from(–)-(*M,R,R),(M,R,R*)-**137a** form a linear complex of Ni^0)

Although $Ni(cod)_2$ is a commonly used source of Ni^0, it requires very careful handling under inert atmosphere in a glove box as it decomposes easily due to its air instability. In order to avoid problems arising from this fact, $Ni(acac)_2$ was chosen as a more convenient, bench stable source of Ni^{II}. EtMgCl turned out to be a reagent of choice that instantly reduces Ni^{II} to Ni^0 while simultaneously deprotonating the imidazolium salt, releasing the desired diastereo- and enantiopure NHC ligand. Experimentally, a Schlenk flask was charged with the pre-dried commercial-grade nickel^{II} acetylacetonate and imidazolium salt and solids were dried in vacuum at 80 °C for an hour. Then THF was added followed by ethylmagnesium chloride solution to generate the active Ni^0-NHC complex. Finally, a solution of triyne **43** was added to the reaction mixture to react at room temperature for a couple of hours.



43 (+)-(*P*)-**46**

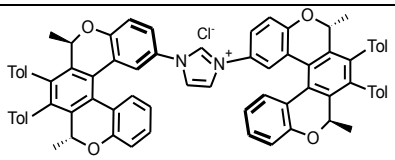
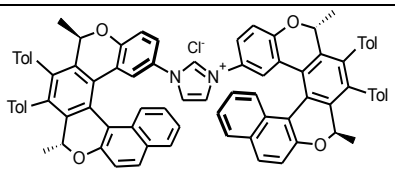
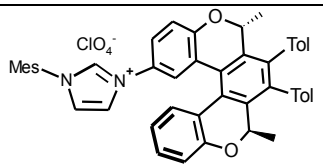
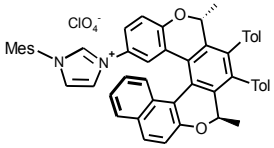
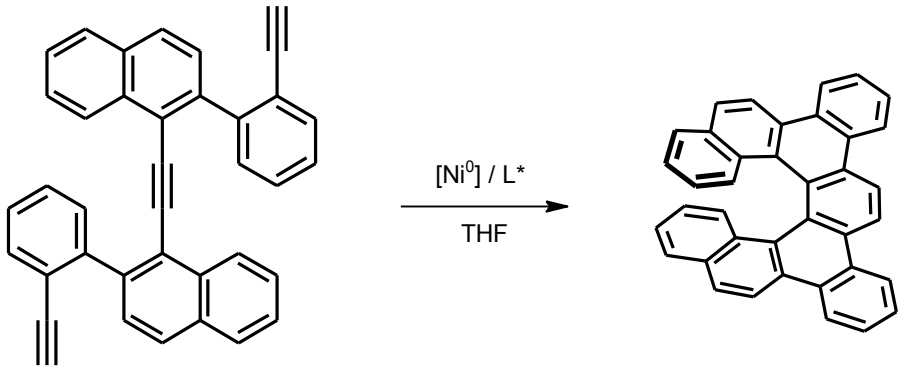
Entry	NHC ligand precursor(L*)	Conversion (%)[a]	*Ee* (%)[a] of (+)-(*P*)-46
1	 (–)-(*M,R,R*),(*M,R,R*)-**136a**	>90	41
2	 (–)-(*M,R,R*),(*M,R,R*)-**137a**	>90	59
3	 (–)-(*M,R,R*)-**138a**	>90	17
4	 (–)-(*M,R,R*)-**139a**	>90	18

Table 1 Nickel catalysed enantioselective [2+2+2] cycloisomerisation of triyne **43** to dibenzo[6]helicene (+)-(*P*)-**46**. $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), (–)-(*M,R,R*),(*M,R,R*)-**136a**, (–)-(*M,R,R*),(*M,R,R*)-**137a**, (–)-(*M,R,R*)-**138a** or (–)-(*M,R,R*)-**139a** (44 mol%), THF, rt, 2 h. [a] Conversion and enantiomeric excess was determined by HPLC on Chiralpak IA

The Ni^0-catalysed intramolecular [2+2+2] cyclotrimerisation of triyne **43** was carried out in the presence of the helical NHC ligands generated *in situ* from the diastereo- and enantiopure imidazolium salts **136a-139a** (**Scheme 35, Scheme 36** and **Scheme 37**) using the aforementioned procedure. The results are summarised in **Table 1**. Uniformly, the use of any imidazolium salt I studied resulted in the formation of the same enantiomer (+)-(*P*)-**46** and, in addition, all reactions proceeded with high conversion. Utilising the symmetrical imidazolium salt derived from oxa[5]helicene (–)-(*M,R,R*),(*M,R,R*)-**136a** gave rise to dibenzo[6]helicene (+)-(*P*)-**46** with 41% *ee* (**Table 1**, Entry 1). The use of a higher homologue, the oxa[6]helicene-derived symmetrical salt (–)-(*M,R,R*),(*M,R,R*)-**137a** led to the enantioenriched (+)-(*P*)-**46** with up to 59% *ee* (**Table 1**, Entry 2). On the other hand, the unsymmetrical mono(oxahelicenyl) imidazolium salts (–)-(*M,R,R*)-**138a** (derived from oxa[5]helicene) and (–)-(*M,R,R*)-**139a** (derived from oxa[6]helicene) were found less efficient in the chirality transfer to receive (+)-(*P*)-**46** with only 17% *ee* (**Table 1**, Entry 3) and 18% *ee* (**Table 1**, Entry 4), respectively. The results clearly demonstrate the remarkable difference between the symmetrical imidazolium salt precursors (–)-(*M,R,R*),(*M,R,R*)-**136a** or (–)-(*M,R,R*),(*M,R,R*)-**137a** *versus* the unsymmetrical imidazolium salt precursors (–)-(*M,R,R*)-**138a** or (–)-(*M,R,R*)-**139a** in the ability to control helicity of the cyclised product. An intuitive explanation may be related to the fact that the increased steric bulkiness of the substituents attached to the NHC carbene ligand could significantly restrict conformational freedom around the metal centre of a key reactive intermediate in which the chirality transfer takes place.

3.2.2 Enantioselective catalysis in the synthesis of nonracemic dibenzo[7]helicene

The disappointingly low enantioselectivity of Ni^0-catalysed [2+2+2] cycloisomerisation in the case of the unsymmetrical mono(oxahelicenyl) imidazolium salts (–)-(*M,R,R*)-**138a** or (–)-(*M,R,R*)-**139a** dismissed this class of NHC ligands from further studies. Therefore, in the following studies I have focused only on symmetrical NHC ligands. To this end, the symmetrical diastereo- and enantiopure bis(oxahelicenyl) salts (–)-(*M,R,R*),(*M,R,R*)-**136a** and (–)-(*M,R,R*),(*M,R,R*)-**137a** were used in Ni^0-catalysed enantioselective [2+2+2] cyclotrimerisation of triyne **160** (prepared previously in our laboratory)[58] to provide nonracemic dibenzo[7]helicene (+)-(*P*)-**161** (**Table 2**). Although the conversions were slightly lower than those obtained for dibenzo[6]helicene (+)-(*P*)-**46**, the enantioselectivities increased significantly. Bis(oxa[5]helicenyl) salt (–)-(*M,R,R*),(*M,R,R*)-**136a** provided (+)-(*P*)-**161** with 72% *ee* (**Table 2**, Entry 1) and bis(oxa[6]helicenyl) salt (–)-(*M,R,R*),(*M,R,R*)-**137a** afforded 74% *ee* (**Table 2**, Entry 2).



160 (+)-(*P*)-**161**

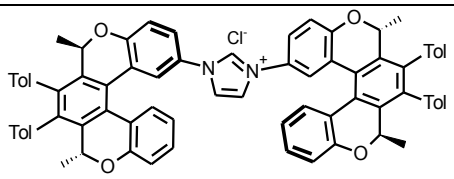
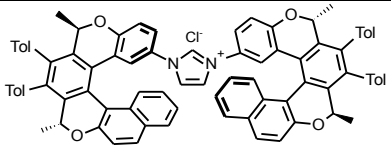
Entry	NHC ligand precursor (L*)	Conversion (%)[a]	*Ee* (%)[a] of (+)-(*P*)-**161**
1	 (–)-(*M,R,R*),(*M,R,R*)-**136a**	64	72
2	 (–)-(*M,R,R*),(*M,R,R*)-**137a**	76	74

Table 2 Nickel catalysed enantioselective [2+2+2] cycloisomerisation to (+)-(*P*)-**161**. $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), (–)-(*M,R,R*),(*M,R,R*)-**136a** or (–)-(*M,R,R*),(*M,R,R*)-**137a** (44 mol%), THF, rt, 2 h. [a] Conversion and enantiomeric excess was determined by HPLC on Chiralpak IA

3.3 SYNTHESIS OF MODIFIED BISOXAHELICENYL NHC LIGANDS BEARING ONE STEREOCENTRE IN THE SKELETON

It is difficult to propose the correct geometry of an intermediary species/transition state controlling the stereochemical outcome of the multistep alkyne [2+2+2] cycloisomerisation process catalysed by chiral metal complexes. However, I found that a relatively small structural change in the NHC ligand can have a profound effect on enantioselectivity of the reaction, as demonstrated by the results of the catalytic experiments presented so far (*cf.* Entries 1 and 2, **Table 1**). Therefore, this requires a more systematic study on the influence of structural modifications of oxahelicene NHC ligands on chirality transfer in this particular enantioselective reaction. First, to understand the individual role of the three elements of chirality present in the oxahelicene NHC ligands, *i.e.*, two chiral centres along with the helix itself, two new chiral NHC precursors were designed. To this end, I always removed just one stereogenic centre from the oxa[5]helicene units of the corresponding symmetrical imidazolium salts so that the remaining stereogenic centre was either closer to or distant from the central imidazolium nucleus, as in (–)-(*M,R*),(*M,R*)-**162** and (–)-(*M,R*),(*M,R*)-**163**, respectively (**Figure 18**).

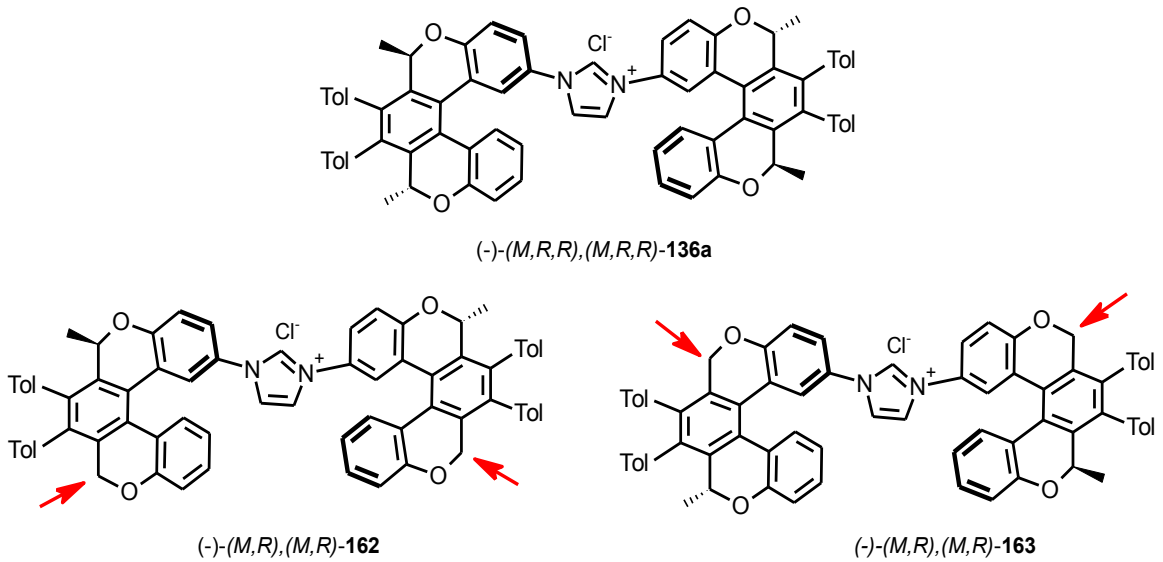
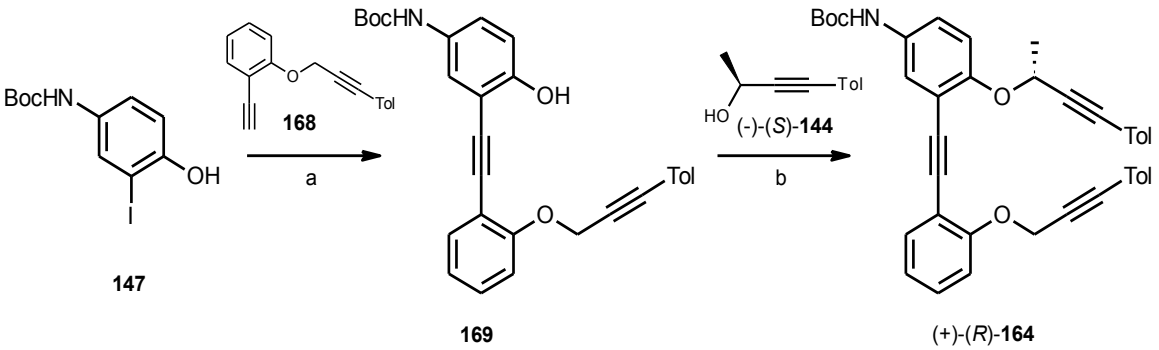


Figure 18 (–)-(*M,R,R*),(*M,R,R*)-**136a** *vs* (–)-(*M,R*),(*M,R*)-**162** and (–)-(*M,R*),(*M,R*)-**163** with reduced number of stereogenic centres (indicated by the red arrows)

3.3.1 Synthesis of the modified 2-aminooxa[5]helicenes

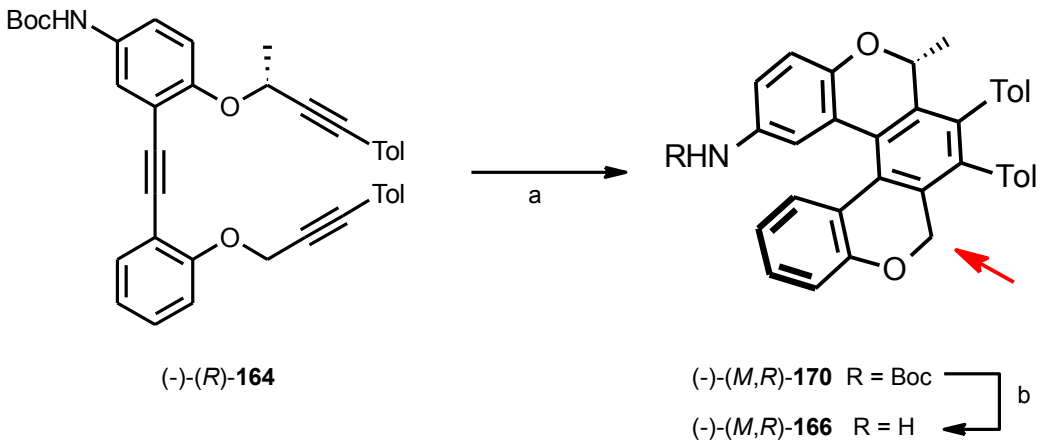
The same versatile methodology for the synthesis of diastereo- and enantiopure oxahelicenes discussed above was employed in the preparation of the centrally chiral triynes (+)-(*R*)-**164** and (–)-(*R*)-**165** (**Scheme 38** and **Scheme 40,** respectively). After cyclisation, they gave rise to the modified oxa[5]helicenes (–)-(*M,R*)-**166** and (–), (*M,R*)-**167** (**Scheme 39** and **Scheme 41,** respectively), making use of the already prepared building blocks (–)-(*R*)-**145**, **147** and (–)-(*S*)-**144** (**Scheme 30**).



Scheme 38 (a) **168** (1.2 equiv.), $PdCl_2(PPh_3)_2$ (4 mol%), CuI (8 mol%), *i*-Pr_2NH (1.2 equiv.), toluene, rt, 16 h, 99%; (b) (–)-(*S*)-**144** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 16 h, 89%.

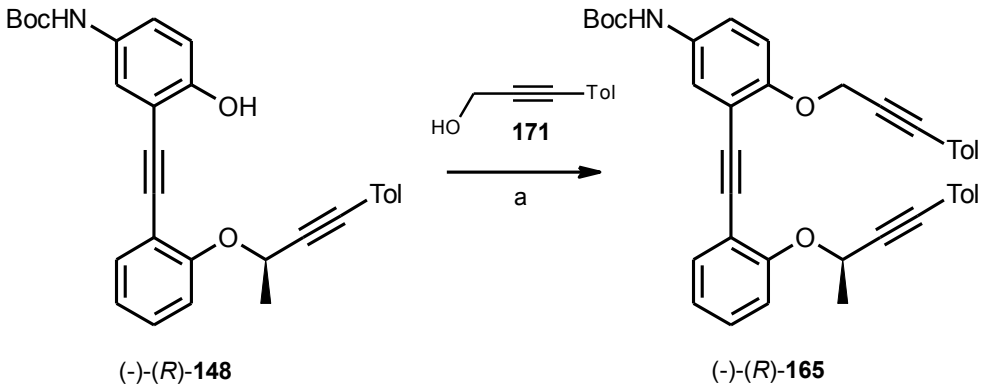
Diyne **168**, synthesised according to literature,[63] was reacted with aryl iodide **147** under Sonogashira reaction conditions to deliver diyne phenol **169**. For the sake of introducing a stereogenic centre of the known absolute configuration into the target triyne, the prepared diyne phenol **169** and enantiopure propargylic alcohol (–)-(*S*)-**144** were subjected to Mitsunobu reaction to afford triyne (+)-(*R*)-**164** with the inversed configuration at the stereogenic centre (**Scheme 38**). Triyne (+)-(*R*)-**164** then underwent the diastereoselective [2+2+2] cyclotrimerisation catalysed by CpCo(CO)(fum) under microwave irradiation, which afforded the diastereo- and enantiopure Boc-protected 2-amino[5]oxahelicene (–)-(*M,R*)-**170** in agreement with our earlier observations.[64] In the last step, trifluoroacetic acid

cleaved the Boc protecting group to liberate 2-aminooxa[5]helicene (–)-(*M,R*)-**166** comprising only a single stereogenic centre along with the element of helical chirality (**Scheme 39**).



Scheme 39 (a) CpCo(CO)(fum) (32 mol%), μW, THF, [bdmim]BF_4, 140 °C, 15 min, 60%; (b) TFA (15.0 equiv.), CH_2Cl_2, rt, 16 h, 76%.

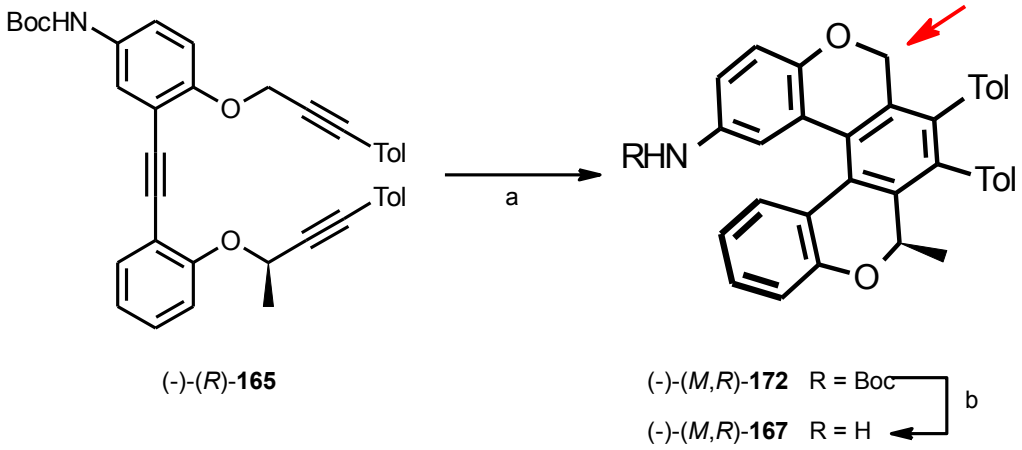
Analogously, the complementary triyne (–)-(*R*)-**165** with the stereogenic centre placed at the other tether was synthesised from the already prepared hydroxydiyne (–)-(*R*)-**148** (**Scheme 30**). 3-(*p*-Tolyl)prop-2-yn-1-ol **171**, prepared from prop-2-yn-1-ol and 1-iodo-4-methylbenzene under Sonogashira reaction conditions similar to those reported in the literature,[163] was subjected to Mitsunobu reaction with phenol (–)-(*R*)-**148** to afford the target triyne (–)-(*R*)-**165** (**Scheme 40**).



(-)-(*R*)-**148** (-)-(*R*)-**165**

Scheme 40 (a) **171** (1.5 equiv.), PPh_3 (1.5 equiv.), DIAD (1.5 equiv.), benzene, rt, 16 h, 83%.

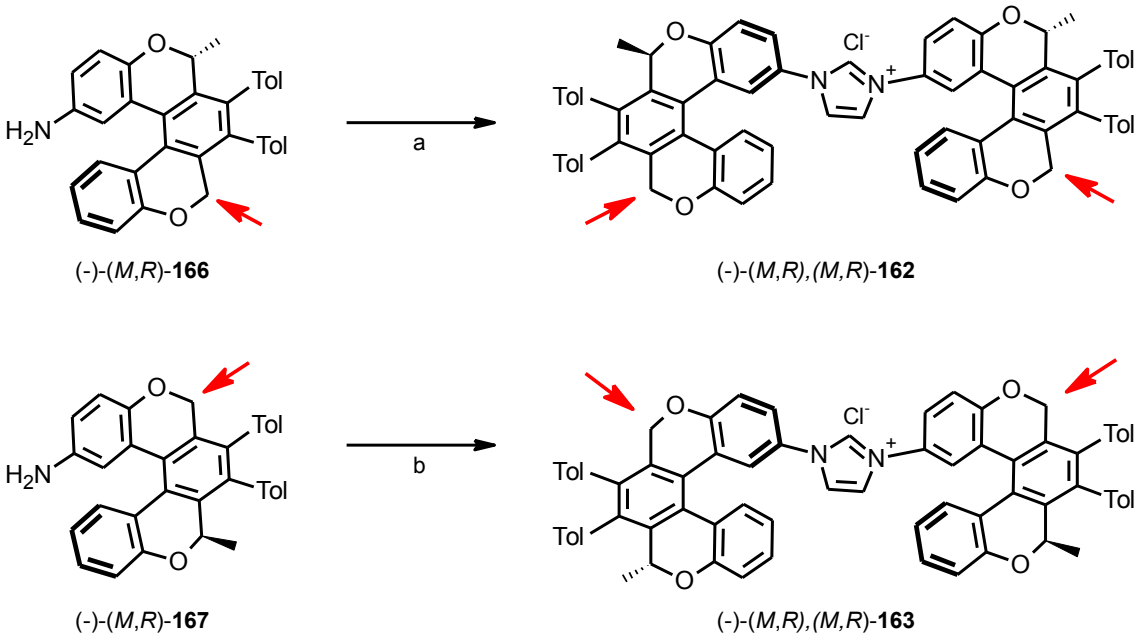
Triyne (–)-(*R*)-**165** was cyclised to the Boc-protected diastereo- and enantiopure oxa[5]helicene (–)-(*M,R*)-**172** employing the Co^I-catalysed [2+2+2] cyclotrimerisation. Again, no trace of the undesired diastereoisomer (*P,R*)-**172** was detected. Trifluoroacetic acid was used to remove the Boc protecting group providing another modified 2-aminooxa[5]helicene (–)-(*M,R*)-**167** in good yield (**Scheme 41**).



Scheme 41 (a) CpCo(CO)(fum) (33 mol%), µW, THF, [bdmim]BF_4, 140 °C, 15 min, 67%; (b) TFA (16.0 equiv.), CH_2Cl_2, rt, 7 h, 80%.

3.3.2 Synthesis of the modified oxa[5]helicene symmetrical imidazolium salts

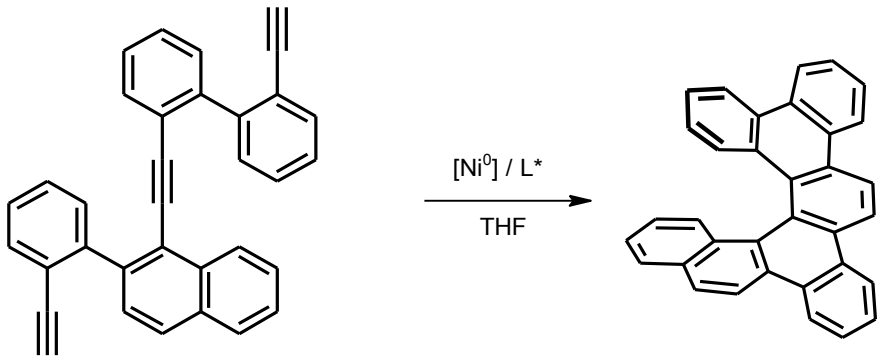
To accomplish synthesis of the symmetrical imidazolium salts (–)-(*M,R*),(*M,R*)-**162** and (–)-(*M,R*),(*M,R*)-**163**, the conditions described in **Section 3.1.2** were successfully applied and the corresponding bis(oxa[5]helicenyl) NHC precursors were obtained in moderate yields. (**Scheme 42**). Depicted in red are the 2*H*-pyran rings where the stereogenic centre has been removed with respect to the parent (–)-(*M,M,R*),(*M,M,,R*)-**136a** discussed above (**Figure 18**).



Scheme 42 (a) (–)-(*M,R*)-**166**, glyoxal aq. (0.5 equiv.), formaldehyde aq. (0.5 equiv.), AcOH, 45 °C, 37 min, 62%; (b) (–)-(*M,R*)-**167**, glyoxal aq. (0.5 equiv.), formaldehyde aq. (0.5 equiv.), AcOH, 45 °C, 42 min, 55%.

3.3.3 Application of modified oxa[5]helicene imidazolium salt in the enatioselective catalysis of nonracemic dibenzo[6]helicene

The symmetrical diastereo- and enantiopure imidazolium salts (–)-(*M,R*),(*M,R*)-**162** and (–)-(*M,R*),(*M,R*)-**163** were applied in the model asymmetric Ni^0-catalysed [2+2+2] cycloisomerisation of tryine **43** to dibenzo[6]helicene **46** (**Scheme 14**). Results are summarised in **Table 3**. The modified bis(oxa[5]helicenyl) NHC ligands generated from precursors (–)-(*M,R*),(*M,R*)-**162** and (–)-(*M,R*),(*M,R*)-**163** afforded the nonracemic (+)-(*P*)-**46** with 90% conversion. The observed enantioselectivity of the cyclisations was more revealing. The use of chiral imidazolium salt (–)-(*M,R*),(*M,R*)-**162** resulted in 36% *ee* of (+)-(*P*)-**46** (**Table 3**, Entry 1) *versus* 41% *ee* of (+)-(*P*)-**46** when (–)-(*M,R,R*),(*M,R,R*)-**136a** was used (**Table 3**, Entry 3). This result showed that the presence of a stereogenic centre placed at the distant position from the core NHC unit does not have much influence on the chirality transfer during the catalytic process. On the contrary, using the imidazolium salt (–)-(*M,R*),(*M,R*)-**163**, which lacks the stereogenic centre in the position closer to the imidazolium core, resulted in the formation of (+)-(*P*)-**46** with just 10% *ee* (**Table 3**, Entry 2). Clearly, the steric congestion caused by the methyl groups in the vicinity of the catalytic centre can play an important role in the mechanism of enantiomeric discrimination.



43 (+)-(*P*)-**46**

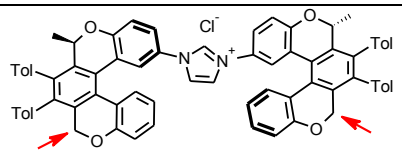
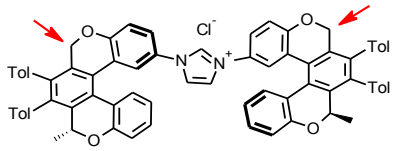
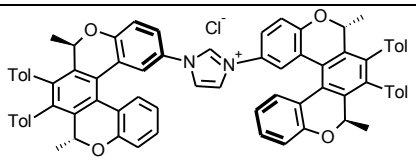
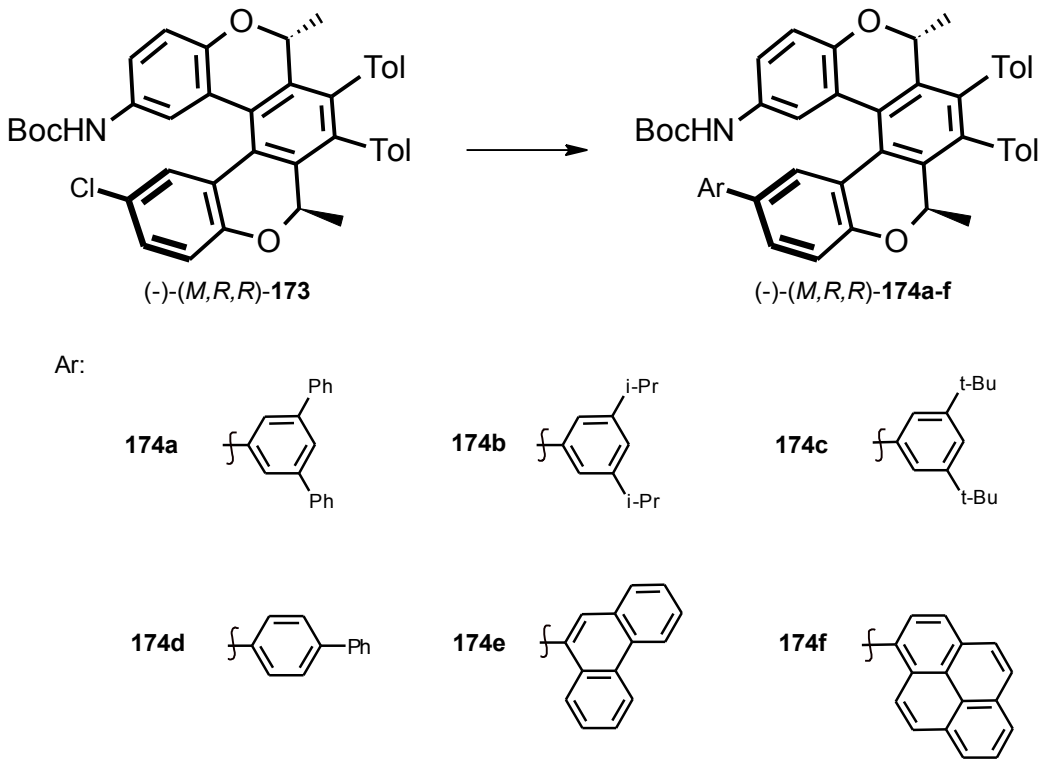
Entry	NHC ligand precursor (L*)	Conversion (%)[a]	*Ee* (%)[a] of (+)-(*P*)-46
1	 (–)-(*M,R*),(*M,R*)-**162**	>90	36
2	 (–)-(*M,R*),(*M,R*)-**163**	>90	10
3[b]	 (–)-(*M,R,R*),(*M,R,R*)-**136a**	>90	41

Table 3 $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), (–)-(*M,R*),(*M,R*)-**162** or (–)-(*M,R*),(*M,R*)-**163** (44 mol%), THF, rt, 2 h. [a] Conversion and enantiomeric excess was determined by HPLC on Chiralpak IA. [b] Result obtained in Section **3.2.1 Table 1**.

3.4 SYNTHESIS OF NHC LIGANDS BASED ON ARYL SUBSTITUTED OXA[5]HELICENE

Considering the results from **Table 3**, both stereogenic centres with the methyl groups occupying the pseudoaxial position have since been retained in the design of all other ligands. In addition, the level of enantioselectivity observed in the experiments with the bis(oxahelicenyl) NHC precursors (–)-(*M,R,R*),(*M,R,R*)-**136a** and (–)-(*M,R,R*),(*M,R,R*)-**137a** (Sections **3.2.1** and **3.2.2**) indicated that the extension of the helicene scaffold by one ring can lead to the more efficient chirality transfer in the studied enantioselective cyclisation.

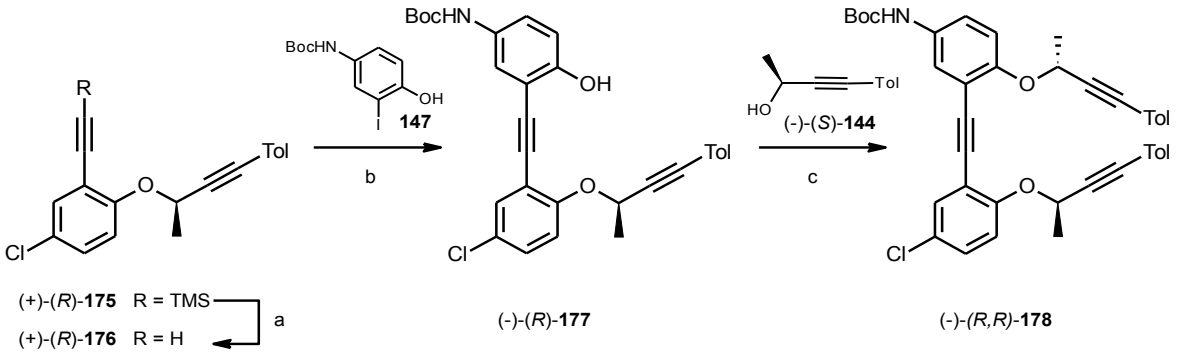
Therefore, the Boc-protected 2-aminooxa[5]helicene (–)-(*M,R,R*)-**173** bearing the chlorine atom in the proper position was chosen as another synthetic target. I assumed that it would allow the modular introduction of various bulky substituents to the desired position, thus mimicking another benzene ring of the oxa[6]helicene backbone of (–)-(*M,R,R*),(*M,R,R*)-**137a**. Due to a low reactivity of the chlorine substituent throughout the multi-step synthesis and its facile displacement in Suzuki-Miyaura reaction, a small library of sterically modified 2-aminooxa[5]helicenes could be generated at a late stage of the synthetic sequence (**Scheme 43**).



Scheme 43 Target chlorinated 2-aminooxa[5]helicene (–)-(*M,R,R*)-**173** and its proposed transformation to the sterically more congested derivatives (–)-(*M,R,R*)-**174a-f**

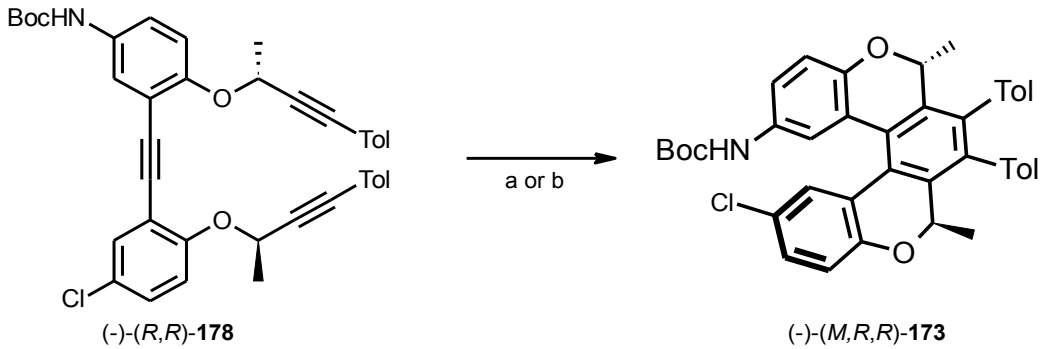
3.4.1 Synthesis of aryl substituted oxa[5]helicenes

The synthesis of chlorinated 2-aminooxa[5]helicene (–)(*M,R,R*)-**173** (**Scheme 43**) started from the commercially available 4-chlorophenol, which was transformed into the silyl-protected (+)-(*R*)-**175**.[164] The silyl-protected building block (+)-(*R*)-**175** was desilylated to afford diyne (+)-(*R*)-**176** in high yield (**Scheme 44**). The two building blocks, diyne (+)-(*R*)-**176** and the functionalised aryl iodide **147**, were cross-coupled under Sonogashira reaction conditions to provide hydroxy diyne (–)-(*R*)-**177** carrying the Boc-protected amino group. It was subjected to Mitsunobu reaction, leading to triyne (–)-(*R,R*)-**178** (**Scheme 44**).



Scheme 44 (a) K_2CO_3 (2.0 equiv.), MeOH, rt, 2 h, 93%. (b) (+)-(*R*)-**176** (1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), *i*-Pr_2NH (1.2 equiv.), toluene, rt, 3 h, 81%; (c) (–)-(*S*)-**144** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 3 h, 77%.

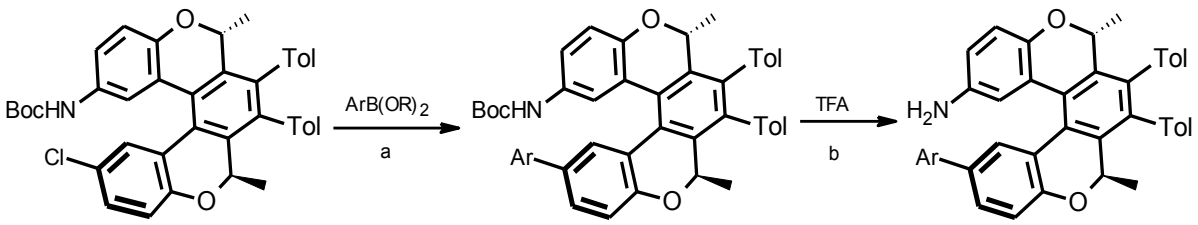
Finally, the key triyne (–)-(*R,R*)-**178** underwent [2+2+2] cyclotrimerisation catalysed by CpCo(CO)(fum) under microwave irradiation that generated the desired diastereo- and enantiopure chloro derivative of oxa[5]helicene (–)-(*M,R,R*)-**173** in moderate yield. Alternatively, the same transformation was accomplished by using $Ni(CO)_2(PPh_3)_2$ as a bench-stable Ni^0 catalyst under conventional heating instead of the microwave irradiation (**Scheme 45**).



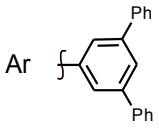
(-)-(*R*,*R*)-**178** (-)-(*M*,*R*,*R*)-**173**

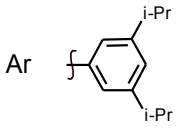
Scheme 45 (a) CpCo(CO)(fum) (50 mol%), μW, THF, [bdmim]BF_4, 140 °C, 15 min, 74%; (b) $Ni(CO)_2(PPh_3)_2$ (36 mol%), toluene, 110 °C, 15 min, 70%.

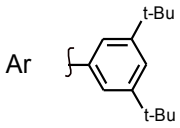
Next, bulky aryl substituents were introduced by Suzuki-Miyaura reaction of the chloro derivative (–)-(*M,R,R*)-**173** with a series of commercially available arylboronic acids or those synthesised according to the literature (**Scheme 46**). It is worth noting that I used Buchwald's second-generation catalyst XPhos Pd G2 as it is widely used for its ability to activate chloro derivatives in the carbon-carbon bond-forming reactions.[165,166] The Suzuki-Miyaura coupling proceeded smoothly providing the arylated Boc-protected 2-aminooxa[5]helicenes (–)-(*M,R,R*)-**174a-f** in good to high yields (**Scheme 46**). The removal of the Boc protecting group with trifluoroacetic acid afforded the free amino derivatives **179a – 179f** in good yields as well.



(-)-(*M*,*R*,*R*)-**173** (-)-(*M*,*R*,*R*)-**174a-f** (-)-(*M*,*R*,*R*)-**179a-f**



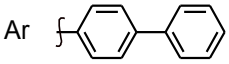


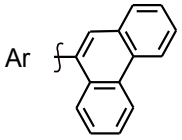


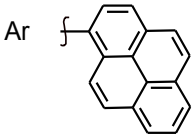
(-)-(*M*,*R*,*R*)-**174a** R = Boc 79%
(-)-(*M*,*R*,*R*)-**179a** R = H 97%

(-)-(*M*,*R*,*R*)-**174b** R = Boc 89%
(-)-(*M*,*R*,*R*)-**179b** R = H 98%

(-)-(*M*,*R*,*R*)-**174c** R = Boc 82%
(-)-(*M*,*R*,*R*)-**179c** R = H 85%







(-)-(*M*,*R*,*R*)-**174d** R = Boc 87%
(-)-(*M*,*R*,*R*)-**179d** R = H 78%

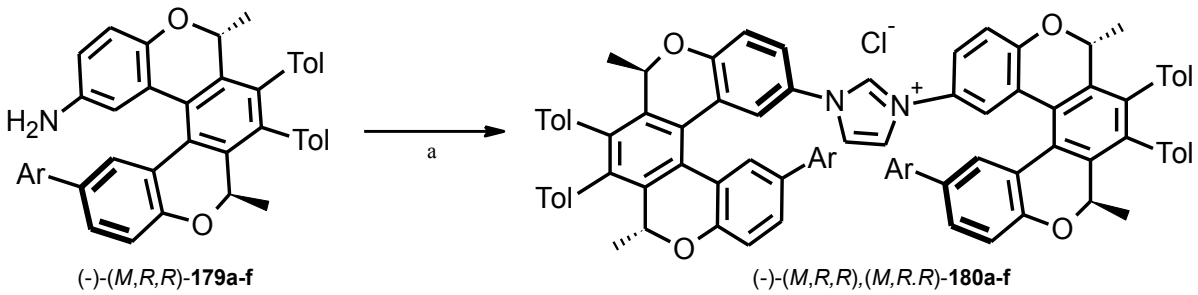
(-)-(*M*,*R*,*R*)-**174e** R = Boc 89%
(-)-(*M*,*R*,*R*)-**179e** R = H 76%

(-)-(*M*,*R*,*R*)-**174f** R = Boc 82%
(-)-(*M*,*R*,*R*)-**179f** R = H 86%

Scheme 46 (a) $ArB(OR)_2$ (2.1 - 3.3 equiv.), XPhos Pd G2 (5 - 8 mol%), K_3PO_4 (0.5 M in water, 1.1 - 2.5 equiv.), THF, 100 °C, 1 - 6 h, (79 - 89%); (b) TFA (15 - 33 equiv.), CH_2Cl_2, rt, 3 - 16 h, (76 - 98%).

3.4.2 Synthesis of aryl substituted oxa[5]helicene symmetrical imidazolium salts

All substituted 2-aminooxa[5]helicenes (–)-(*M,R,R*)-**179a-f** were converted into the symmetrical bis(oxa[5]helicenyl) imidazolium salts (–)-(*M,R,R*),(*M,R,R*)-**180a-f** under the conditions I described earlier (acid-catalysed condensation of primary amines with glyoxal and formaldehyde; **Scheme 47**). The results of these transformations are summarised in **Table 4**. Notably, all of the bis(oxa[5]helicenyl) imidazolium salts (–)-(*M,R,R*),(*M,R,R*)-**180a-f** were obtained in good to high yields.



(-)-(*M,R,R*)-**179a-f** (-)-(*M,R,R*),(*M,R.R*)-**180a-f**

Scheme 47 (a) (–)-(*M,R,R*)-**179a-f**, glyoxal aq. (0.5 - 0.6 equiv.), formaldehyde aq. (0.5 - 0.8 equiv.), AcOH, 45-55 °C, 0.7 - 3.7 h.

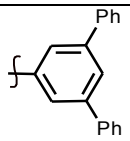
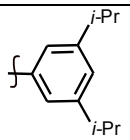
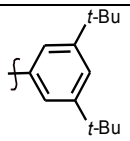
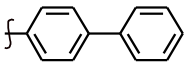
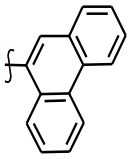
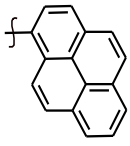
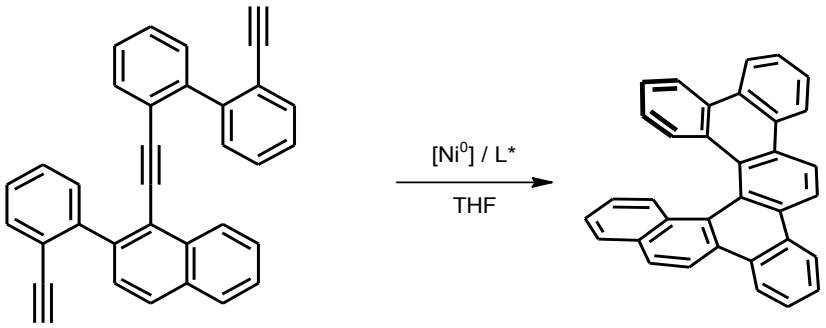
Entry	Ar	Educt	Product	Yield (%)
1		(–)-(*M,R,R*)-**179a**	(–)-(*M,R,R*),(*M,R,R*)-**180a**	57
2		(–)-(*M,R,R*)-**179b**	(–)-(*M,R,R*),(*M,R,R*)-**180b**	64
3		(–)-(*M,R,R*)-**179c**	(–)-(*M,R,R*),(*M,R,R*)-**180c**	82
4		(–)-(*M,R,R*)-**179d**	(–)-(*M,R,R*),(*M,R,R*)-**180d**	83
5		(–)-(*M,R,R*)-**179e**	(–)-(*M,R,R*),(*M,R,R)*-**180e**	82
6		(–)-(*M,R,R*)-**179f**	(–)-(*M,R,R*),(*M,R,R*)-**180f**	61

Table 4 Symmetrical bisoxa[5]helicenyl imidazolium salts (–)-(*M,R,R*),(*M,R,R*)-**180a-f**

3.4.3 Application of aryl substituted oxa[5]helicene symmetrical imidazolium salt in the enantioselective catalysis of nonracemic dibenzo[6]helicene

The six new symmetrical bis(oxa[5]helicenyl) imidazolium salts (–)-(*M,R,R*),(*M,R,R*)-**180a-f** were applied in the model reaction, the enantioselective intramolecular Ni^0-catalysed [2+2+2] cycloisomerisation of aromatic triyne **43** to nonracemic dibenzo[6]helicene (+)-(*P*)-**46** (**Table 5**). All the reactions gave the enantiorenriched helicene (+)-(*P*)-**46**. The conversions ranged from 73% to 90% (**Table 5**, Entry 1 - 6), slightly lower than those with (–)-(*M,R,R*),(*M,R,R*)-**136a** (**Table 5**, Entry 7).



43 (+)-(*P*)-**46**

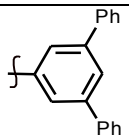
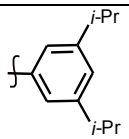
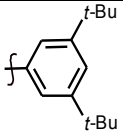
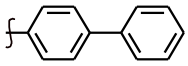
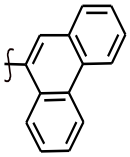
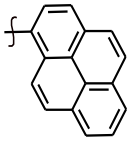
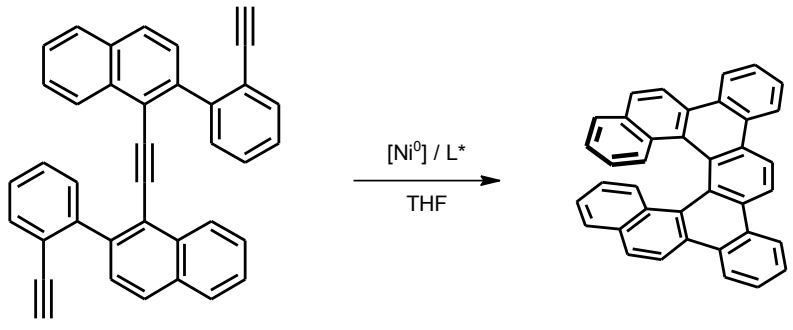
Entry	Ar	NHC ligand precursor (L*)	Conversion (%)[a]	Ee (%)[a] of 46
1		(–)-(*M,R,R*),(*M,R,R*)-**180a**	90	61
2		(–)-(*M,R,R*),(*M,R,R*)-**180b**	90	64
3		(–)-(*M,R,R*),(*M,R,R*)-**180c**	81	66
4		(–)-(*M,R,R*),(*M,R,R*)-**180d**	89	44
5		(–)-(*M,R,R*),(*M,R,R*)-**180e**	73	56
6		(–)-(*M,R,R*),(*M,R,R*)-**180f**	90	47
7[b]	H	(–)-(*M,R,R*),(*M,R,R*)-**136a**	>90	41

Table 5 $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), (–)-(*M,R,R*),(*M,R,R*)-**180a-f** (44 mol%), THF, rt, 2 h. **[a]** Conversion and enantiomeric excess was determined by HPLC on Chiralpak IA. **[b]** See Section **3.2.1**, **Table 1**.

Most importantly, the use of all the substituted NHC ligand precursors (–)-(*M,R,R*),(*M,R,R*)-**180a-f** led to the higher enantiomeric excess of (+)-(*P*)-**46** than in the case of (–)-(*M,R,R*),(*M,R,R*)-**136a** (**Table 5**). From the results we could learn that ligands generated from the imidazolium salts (–)-(*M,R,R*),(*M,R,R*)-**180a**, (–)-(*M,R,R*),(*M,R,R*)-**180b** and (–)-(*M,R,R*),(*M,R,R*)-**180c** (**Table 5**, Entries 1, 2 and 3), which possess 3,5-disubstituted 1-aryl substituents, expressed more efficient chirality transfer (61% *ee*, 64% *ee* and 66% *ee*, respectively). In contrast, the use of (–)-(*M,R,R*),(*M,R,R*)-**180d**, which bears the 4-substituted aryl group, resulted in a lower enantiomeric excess of (+)-(*P*)-**46** (44% *ee*; **Table 5**, Entry 4). The presence of more extended aryl substituents, such as phenanthren-9-yl or pyren-1-yl, in the bis(oxa[5]helicenyl) imidazolium salts (–)-(*M,R,R*),(*M,R,R*)-**180e** and (–)-(*M,R,R*),(*M,R,R*)-**180f**, respectively, led to moderate enantiomeric excess of (+)-(*P*)-**46** (56% *ee* and 47% *ee*, respectively; **Table 5**, Entries 5 and 6).

3.4.4 Application of aryl substituted oxa[5]helicene symmetrical imidazolium salt in the enantioselective catalysis of nonracemic dibenzo[7]helicene

The successful bis(oxa[5]helicenyl) imidazolium salt (–)-(*M,R,R*),(*M,R,R*)-**180b** was also tested in the enantioselective Ni^0-catalysed [2+2+2] cyclotrimerisation of the aromatic triyne **160** to provide the nonracemic dibenzo[7]helicene (+)-(*P*)-**161**. An enantiomeric excess of 86% *ee* was achieved (**Table 6**, Entry 3), which turned out to be superior to either (–)-(*M,R,R*),(*M,R,R*)-**136a** or (–)-(*M,R,R*),(*M,R,R*)-**137a** (**Table 6**, Entries 1 and 2) in terms of reactivity and chirality transfer.



160 (+)-(*P*)-**161**

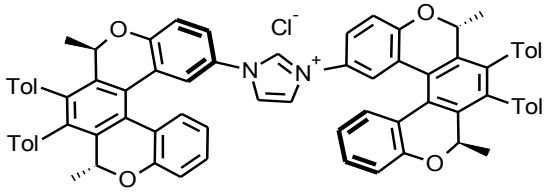
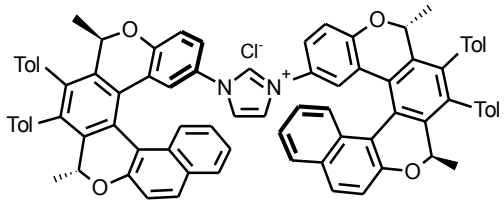
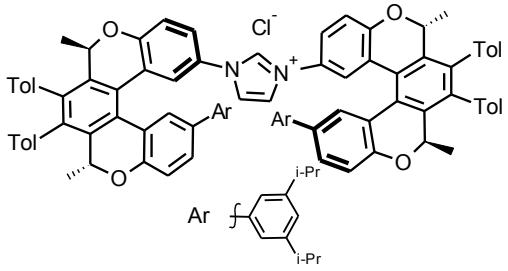
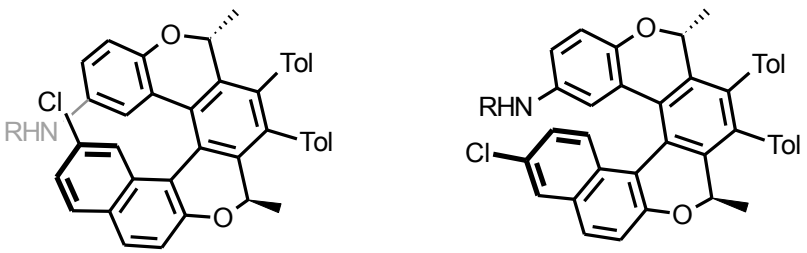
Entry	NHC ligand precursor (L*)	Conversion (%)[a]	Ee (%)[a] of 161
1[b]	 (–)-(*M,R,R*),(*M,R,R*)-**136a**	64	72
2[b]	 (–)-(*M,R,R*),(*M,R,R*)-**137a**	76	74
3	 (–)-(*M,R,R*),(*M,R,R*)-**180b**	**86**	**86**

Table 6 $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), (–)-(*M,R,R*),(*M,R,R*)-**180b** (44 mol%), THF, rt, 2 h. **[a]** Conversion and enantiomeric excess was determined by HPLC on Chiralpak IA. **[b]** See Section **3.2.2**, **Table 2**.

3.5 SYNTHESIS OF NHC LIGANDS BASED ON ARYL SUBSTITUTED OXA[6]HELICENES

Inspired by the fact that the presence of proper aryl substituents in the bis(oxa[5]helicenyl) imidazolium salts as precursors to helical NHC ligands could result in increasing enantiomeric excess of the respective model reaction, enantioselective Ni^0-catalysed [2+2+2] cycloisomerisation, two additional 2-aminooxa[6]helicene building blocks (–)-(*M,R,R*)-**181** and (–)-(*M,R,R*)-**182** were designed and synthesised (**Figure 19**). I suggested combining two positive effects on the enantioselectivity of the study reaction that have already been observed. First, the ligand generated from the imidazolium salt (–)-(*M,R,R*),(*M,R,R*)-**137a**, structurally related to the oxa[6]helicene core, always afforded the higher enantioselectivity than the ligand generated from the imidazolium salt (–)-(*M,R,R*),(*M,R,R*)-**136a**, structurally related to the oxa[5]helicene core. Second, installing an extra aryl substituent on the terminal ring of the oxa[5]helicene scaffold, which is comprised in the NHC ligand precursor such as an imidazolium salt (–)-(*M,R,R*),(*M,R,R*)-**136a**, had also a positive effect on enantioselectivity of the model reaction (*cf*. % *ee*'s obtained with the imidazolium salts (–)-(*M,R,R*),(*M,R,R*)-**180a-f**, **Table 5**). Thus, the extension of the helical backbone along with the attachment of additional aryl substituents to the desired positions appeared to be the next logical step in designing other helical NHC ligands. The synthesis of the chlorinated 2-aminooxa[6]helicene (–)-(*M,R,R*)-**181** and (–)-(*M,R,R*)-**182** (**Figure 19**) followed the strategy already presented in Section **3.4.1**. They were proposed as suitable substrates for Suzuki-Miyaura reaction to introduce aryl substituents in the late stage of the synthesis of the corresponding bis(oxa[6]helicenyl) imidazolium salts as precursors to helical NHC ligands.

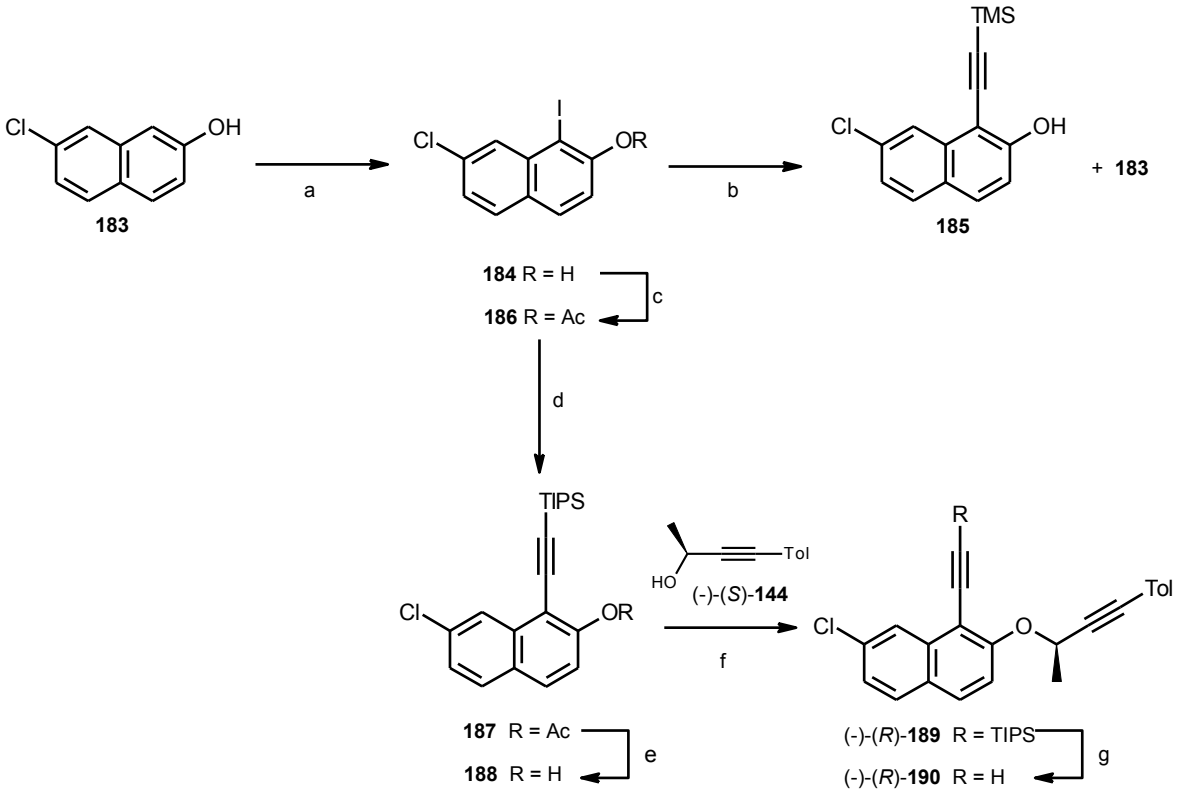


(-)-(*M*,*R*,*R*)-**181** R = Boc (-)-(*M*,*R*,*R*)-**182** R = Boc

Figure 19 Target chlorinated 2-aminooxa[6]helicene (–)-(*M,R,R*)-**181** and (–)-(*M,R,R*)-**182**

3.5.1 Synthesis of modified chloro 2-aminooxa[6]helicenes

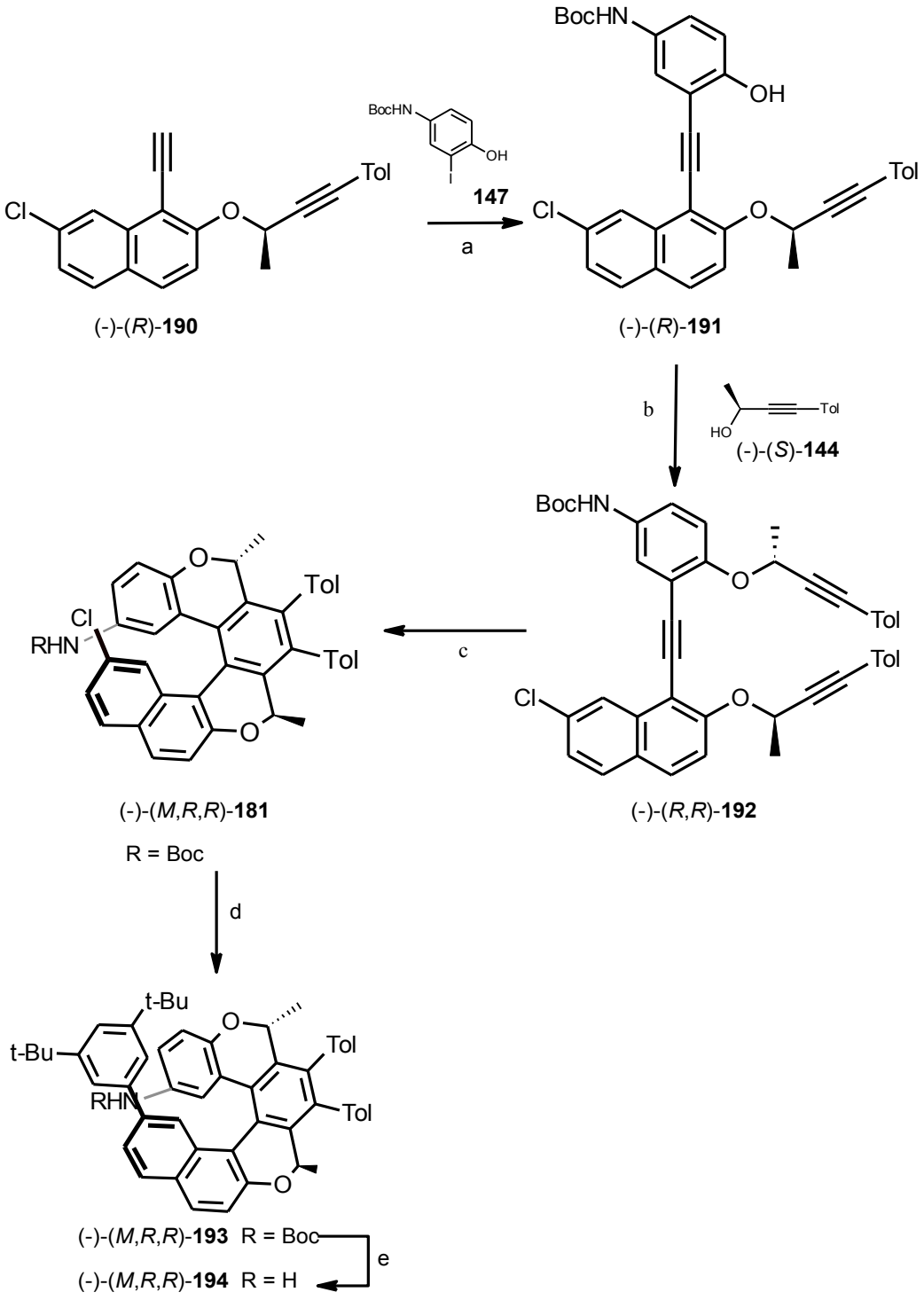
The synthesis of the chlorinated 2-aminooxa[6]helicene derivative (–)-(*M,R,R*)-**181** started from the commercially available 7-chloronaphthalen-2-ol **183**, which was selectively iodinated under basic conditions to 7-chloro-1-iodonaphthalen-2-ol **184**. Since any attempt to substitute the iodine atom in **184** with ethynyltrimethylsilane under Sonogashira conditions led to low yields of **185** (< 4%) and recovery of the deiodinated 7-chloronaphthalen-2-ol **183** (**Scheme 48**), the hydroxy group was first acetylated with acetyl chloride. Then, acetate **186** underwent smoothly Sonogashira reaction with ethynyltriisopropylsilane and afforded the silylated alkyne **187** in good overall yield. Removal of the acetyl protecting group led to the naphthol **188**. In order to introduce the second alkyne unit along with a stereogenic centre of known absolute configuration, the free phenolic group in compound **188** was substituted with the optically pure propargylic alcohol (–)-(*S*)-**144** under Mitsunobu reaction conditions to furnish chiral diyne (–)-(*R*)-**189**. Finally, its desilylation led to the desired enantiopure building block (–)-(*R*)-**190** (**Scheme 48**).



Scheme 48 (a) Na_2CO_3 (2.0 equiv.), I_2 (1.0 equiv.), THF:H_2O (4:1), rt, 4 h, 91%; (b) TMS-C≡CH (1.8 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (4 mol%), *i*-Pr_2NH (1.7 equiv.), toluene, rt, 16 h, 4%; (c) Et_3N (2.5 equiv.), AcCl (1.5 equiv.), CH_2Cl_2, 0 °C to rt, 5 h, 98%; (d) TIPS-C≡CH (1.2 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (5 mol%), *i*-Pr_2NH (1.2 equiv.), toluene, 70 °C, 3 h, then rt for 13 h, 92%; (e) K_2CO_3 (2.0 equiv.), THF-CH_3OH (1:1), rt, 3 h, 97%; (f) (–)-(*S*)-**144** (1.1 equiv.), PPh_3 (1.1 equiv.), DIAD (1.1 equiv.), benzene, rt, 3 h, 78%; (g) *n*-Bu_4NF (1.1 equiv.), THF:CH_3OH (100:1), rt, 1 h, 96%.

The synthesis of the target triyne (–)-(*R,R*)-**192** continued by coupling the Boc-protected aniline **147** with diyne (–)-(*R*)-**190** under Sonogashira reaction conditions to give the phenolic derivative (–)-(*R*)-**191**. It underwent Mitsunobu reaction with the enantiopure alcohol (–)-(*S*)-**144** to provide the chiral triyne (–)-(*R,R*)-**192**. The Co^I-mediated [2+2+2] cycloisomerisation of (–)-(*R,R*)-**192** resulted in the formation of the desired diastereo- and enantiopure 15-chloro-2-aminooxa[6]helicene (–)-(*M,R,R*)-**181** in good yield. Subsequently, its Suzuki-Miyaura coupling with 3,5-di-*tert*-butylphenylboronic acid catalysed by XPhos

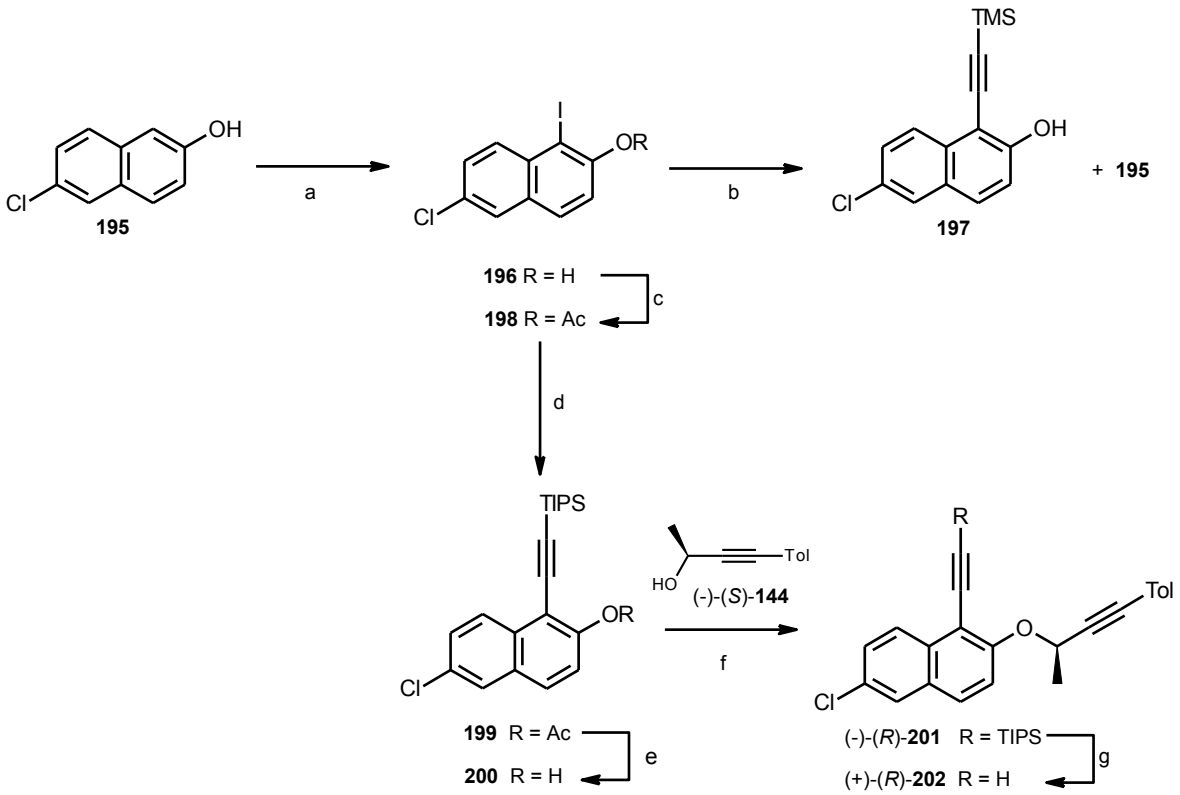
Pd G2 led to the arylated 2-aminooxa[6]helicene (–)-(*M,R,R*)-**193** that, upon removal of the Boc protecting group, furnished the primary amine (–)-(*M,R,R*)-**194** (**Scheme 49**).



Scheme 49 (a) (–)-(*R*)-**190** (1.2 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (4 mol%), *i*-Pr_2NH (1.2 equiv.), toluene, 40 °C, 3.5 h, 75%; (b) (–)-(*S*)-**144** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 3 h, 72%; (c) CpCo(CO)(fum) (43 mol%), μW, THF, $[bdmim]BF_4$, 140 °C, 15 min, 70%; (d) (3,5-di-tert-butylphenyl)boronic acid (2.0 equiv.), XPhos Pd G2 (10 mol%), K_3PO_4 (0.5 M in water, 2.5 equiv.), toluene, 120 °C, 2 h, 86%; (e) TFA (20.0 equiv.), CH_2Cl_2, rt, 16 h, 81%.

Synthesis of target 14-chloro-2-aminooxa[6]helicene (–)-(*M,R,R*)-**182** benefited from the successful preparation of the regioisomeric 15-chloro-2-aminooxa[6]helicene (–)-(*M,R,R*)-**181**. First, the commercially available 6-chloronaphthalen-2-ol **195** was selectively iodinated under basic conditions to receive 6-chloro-1-iodonaphthalen-2-ol **196**. Sonogashira reaction of 6-chloro-1-iodonaphtalen-2-ol **196** with ethynyltrimethylsilane produced compound **197** in 27% yield together with the deiodinated 6-chloronaphthalen-2-ol **195** (**Scheme 50**). Although the yield was significantly higher than in the case of the regioisomer 7-chloro-1-iodonaphthalen-2-ol **184** the free alcohol still had to be protected.

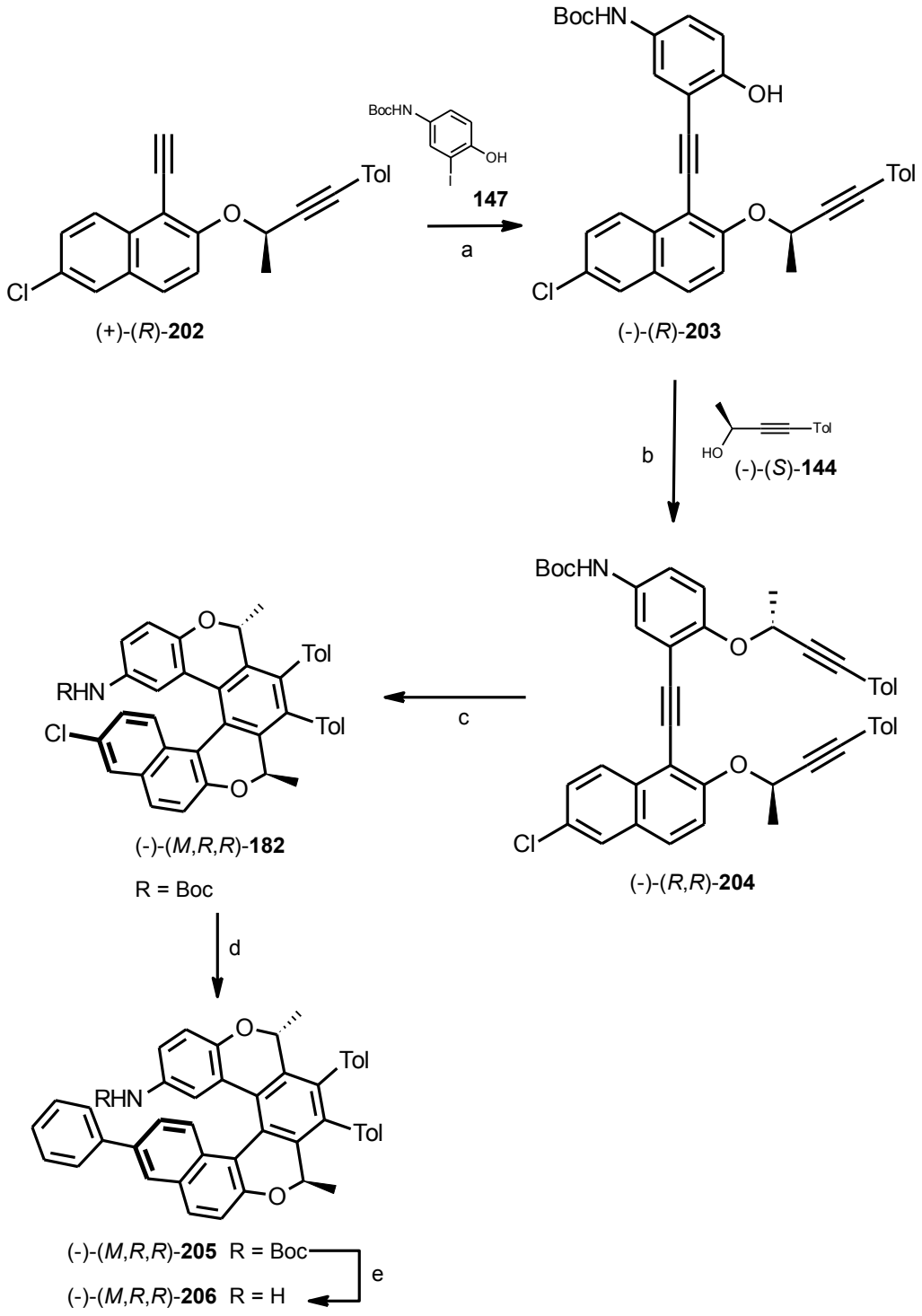
Therefore, 6-chloro-1-iodonaphthalen-2-ol **196** was acetylated by reaction with acetyl chloride before being subjected to Sonogashira reaction with ethynyltriisopropylsilane to give the protected alkyne **199**. After removal of the acetyl protecting group, naphthol **200** was reacted with the chiral alcohol (–)-(*S*)-**144** under Mitsunobu reaction conditions to produce the silylated diyne (–)-(*R*)-**201**. Even though two extra steps were inserted into the synthetic sequence, the overall yield was remarkably high suggesting that the protection of the phenolic group in **196** is clearly an advantage in this synthetic sequence. The cleavage of the triisopropylsilyl group accomplished the preparation of the diyne building block (+)-(*R*)-**202** in good yield (**Scheme 50**).



Scheme 50 (a) Na_2CO_3 (2.0 equiv.), I_2 (1.0 equiv.), THF:H_2O (4:1), rt, 5 h, 96%; (b) TMS-C≡CH (2.0 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (5 mol%), *i*-Pr_2NH (1.4 equiv.), toluene, 40 °C, 2.5 h, 27%; (c) Et_3N (2.1 equiv.), AcCl (1.1 equiv.), CH_2Cl_2, 0 °C to rt, 1.5 h, 98%; (d) TIPS-C≡CH (1.2 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (3 mol%), *i*-Pr_2NH (1.2 equiv.), toluene, 70 °C, 3 h, 94%; (e) K_2CO_3 (2.0 equiv.), THF-CH_3OH (1:1), rt, 3 h, 99%; (f) (–)-(*S*)-**144** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 23 h, 70%; (g) *n*-Bu_4NF (1.2 equiv.), THF:CH_3OH (100:1), rt, 45 min, 99%.

Diyne (+)-(*R*)-**202** was reacted with the functionalised aryl iodide **147** under Sonogashira cross-coupling conditions to form the diyne phenol (–)-(*R*)-**203**. Its Mitsunobu reaction with the enantiopure alcohol (–)-(*S*)-**144** provided the desired chiral triyne (–)-(*R,R*)-**204**. Co^I-catalysed [2+2+2] cycloisomerisation afforded the diastereo- and enantiopure 14-chloro-2-amino[6]oxahelicene (–)-(*M,R,R*)-**182** in good yield (**Scheme 51**). The XPhos Pd G2 promoted the Suzuki-Miyaura cross-coupling reaction of the commercially available phenylboronic acid and the chlorinated oxa[6]helicene derivative (–)-(*M,R,R*)-**182** to deliver

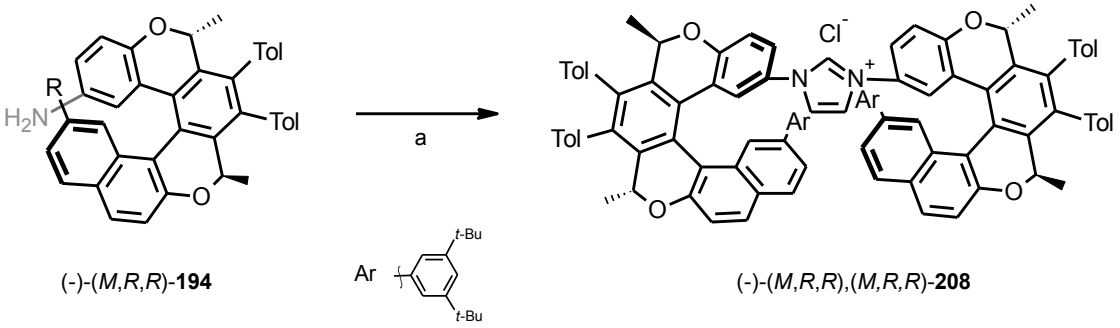
the substituted aminooxa[6]helicene (–)-(*M,R,R*)-**205** in excellent yield. The removal of the Boc protecting group by trifluoroacetic acid provided the desired (–)-(*M,R,R*)-**206** (**Scheme 51**), which served as a precursor for the symmetrical bis(oxa[6]helicenyl) imidazolium salt (–)-(*M,R,R*),(*M,R,R*)-**207** (**Scheme 53**).



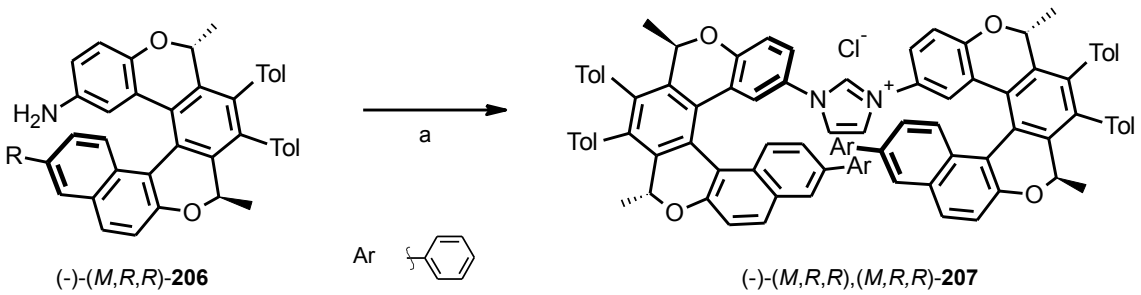
Scheme 51 (a) (+)-(*R*)-**202** (1.2 equiv.), $Pd(PPh_3)_4$ (2 mol%), CuI (5 mol%), *i*-Pr_2NH (1.2 equiv.), toluene, 50 °C, 3 h, 81%; (b) (–)-(*S*)-**144** (1.4 equiv.), PPh_3 (1.3 equiv.), DIAD (1.2 equiv.), benzene, rt, 4 h, 66%; (c) CpCo(CO)(fum) (47 mol%), μW, THF, [bdmim]BF_4, 140 °C, 15 min, 82%; (d) phenylboronic acid (2.8 equiv.), XPhos Pd G2 (10 mol%), aq. K_3PO_4 (0.5 M in water, 2.5 equiv.), THF, 100 °C, 3 h, 96%; (e) TFA (21.0 equiv.), CH_2Cl_2, 16 h, rt, 91%.

3.5.2 Synthesis of aryl substituted oxa[6]helicene symmetrical imidazolium salts

The arylated 2-aminooxa[6]helicene (–)-(*M,R,R*)-**194** and the regioisomeric 2-aminooxa[6]helicene (–)-(*M,R,R*)-**206** reacted with aqueous glyoxal and aqueous formaldehyde under acidic conditions to afford the imidazolium salts (–)-(*M,R,R*),(*M,R,R*)-**208** (**Scheme 52**) and (–)-(*M,R,R*),(*M,R,R*)-**207** (**Scheme 53**) in good yields.



Scheme 52 (a) (–)-(*M,R,R*)-**194**, glyoxal aq. (0.5 equiv.), formaldehyde aq. (0.7 equiv.), AcOH, 55 °C, 35 min, 69%.

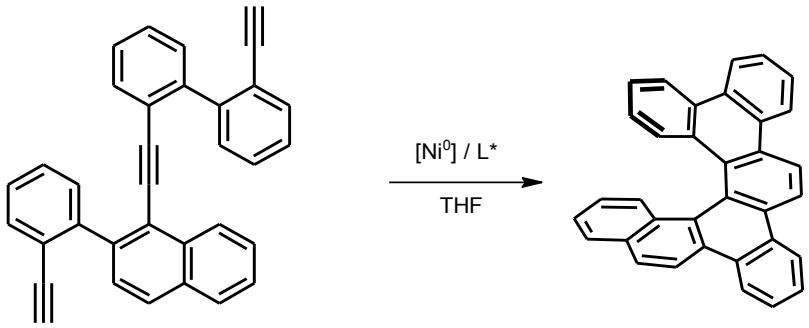


(-)-(*M*,*R*,*R*)-**206** (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**207**

Scheme 53 (a) (–)-(*M,R,R*)-**206**, glyoxal aq. (0.5 equiv.), formaldehyde aq. (0.7 equiv.), AcOH, 55 °C, 46 min, 67%.

3.5.3 Application of aryl substituted oxa[6]helicene symmetrical imidazolium salts in the enatioselective catalysis of nonracemic dibenzo[6]helicene

The arylated bis(oxa[6]helicenyl) salts (–)-(*M,R,R*),(*M,R,R*)-**207** and (–)-(*M,R,R*),(*M,R,R*)-**208** were employed in the enantioselective Ni^0-catalysed [2+2+2] cyclotrimerisation of aromatic triyne **43** leading to the nonracemic dibenzo[6]helicene **46** (**Table 7**). In both cases the optically pure NHC carbene ligands generated from the corresponding imidazolium salts yielded (+)-(*P*)-**46** with moderate to high conversion. Unfortunately, the use of either of these two modified NHC ligand precursors did not lead to increased enantioselectivity of the reaction despite the presence of bulky aryl substituents and the use of the extended oxa[6]helicene scaffold. The NHC ligand bearing 3,5-di-*tert*-butylphenyl substituents in the position 15 of the helical core (**Table 7**, Entry 1) provided the same enantiomeric excess as the parent ligand (**Table 7**, Entry 3), *i.e.* 59% *ee*. More surprisingly, the NHC ligand carrying the phenyl substituent at the position 14 of the helical core (**Table 7**, Entry 2) gave a lower enantiomeric excess than the parent ligand generated from the imidazolium salt (–)-(*M,R,R*),(*M,R,R*)-**137a** (without an extra phenyl substituent), 42% *ee vs* 59% *ee*.



43 (+)-(*P*)-**46**

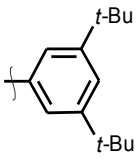
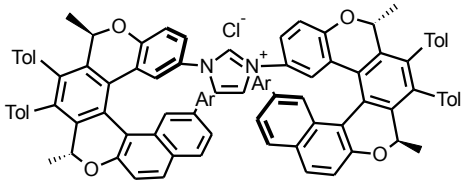
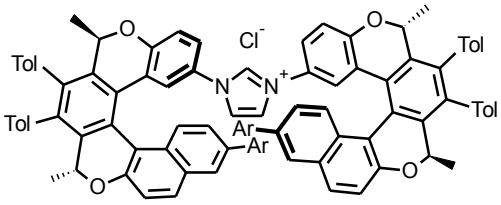
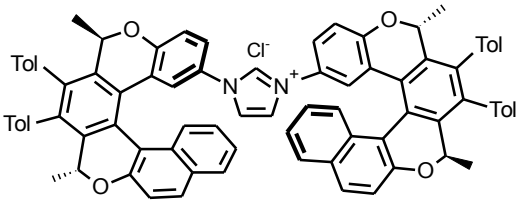
Entry	Ar	NHC ligand precursor (L*)	Conversion (%)[a]	Ee (%)[a] of 46
1		 (–)-(*M,R,R*),(*M,R,R*)-**208**	>90	59
2		 (–)-(*M,R,R*),(*M,R,R*)-**207**	55	42
3[b]	H	 (–)-(*M,R,R*),(*M,R,R*)-**137a**	>90	59

Table 7 $Ni(acac)_2$ (20 mol%), EtMgCl (0.4 M in THF, 0.9 equiv.), (–)-(*M,R,R*),(*M,R,R*)-**207** or (–)-(*M,R,R*),(*M,R,R*)-**208** (44 mol%), THF, rt, 2 h. **[a]** Conversion and enantiomeric excess was determined by HPLC on Chiralpak IA. **[b]** See Section **3.2.1**, **Table 1**.

4 CONCLUSIONS

Aiming at the development of new helically chiral NHC ligands for enantioselective Ni^0-catalysed alkyne [2+2+2] cycloisomerisation to obtain enantioenriched fully aromatic dibenzohelicenes, a series of diastereo- and enantiopure Boc-protected aminooxa[5]- and aminooxa[6]helicenes was synthesised using the well-established metal catalysed diastereoselective alkyne [2+2+2] cycloisomerisation. The helical scaffold of the newly designed NHC ligand precursors was further diversified by introducing sterically demanding aryl substituents in different positions utilising Suzuki-Miyaura reaction of the respective chlorohelicene derivatives and boronic acids. Removal of the Boc-protecting group led to the key aminooxa[5]- and aminooxa[6]helicenes (**Figure 20**), which served as precursors for the synthesis of the corresponding symmetrical and unsymmetrical imidazolium salts (**Figure 21**).

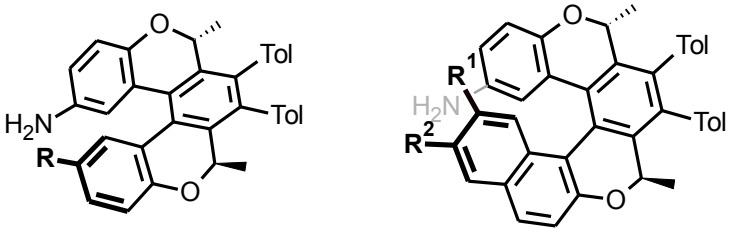
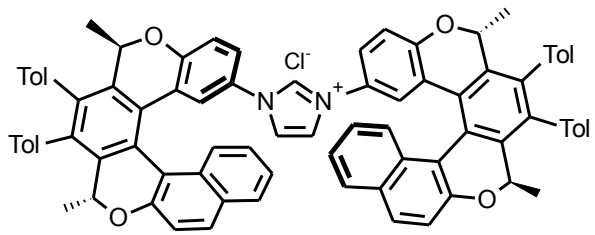
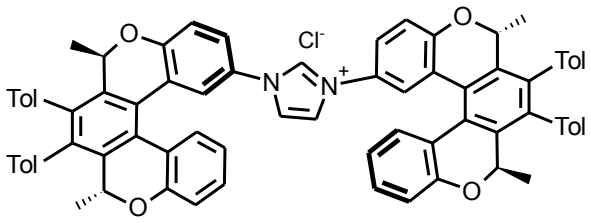


Figure 20 Overview of the synthesised aminooxahelicenes

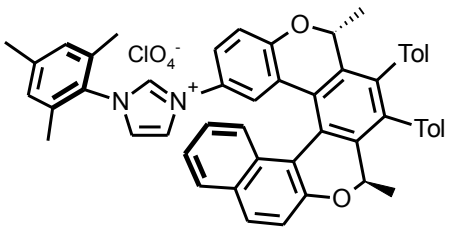
For the first time, the helicene-based N-heterocyclic carbenes generated *in situ* by deprotonation of their corresponding imidazolium salts have been used in the enantioselective Ni^0-catalysed triyne [2+2+2] cyclotrimerisation to dibenzohelicenes. Chirality has been successfully transferred from the novel helically/centrally chiral NHC ligands to the helically chiral dibenzohelicene products, reaching a promising level of enantiodiscrimination: The monitored enantiomeric excess ranged from 41% *ee* to 66% *ee* for dibenzo[6]helicene (+)-(*P*)-**46** and from 72% *ee* to 86% *ee* for dibenzo[7]helicene (+)-(*P*)-**161**.



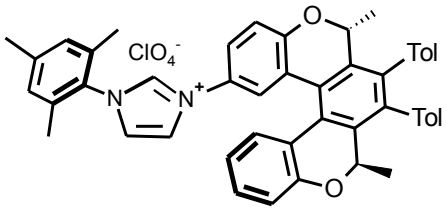
(-)-(*M,R,R*),(*M,R,R*)-**137a**



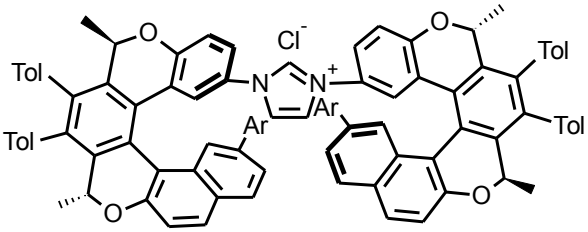
(-)-(*M,R,R*),(*M,R,R*)-**136a**



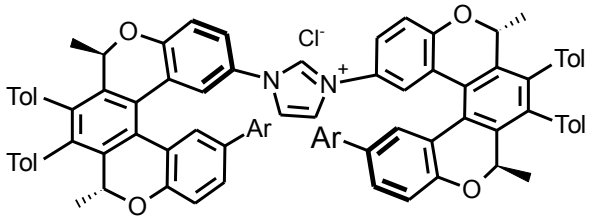
(-)-(*M,R,R*)-**138a**



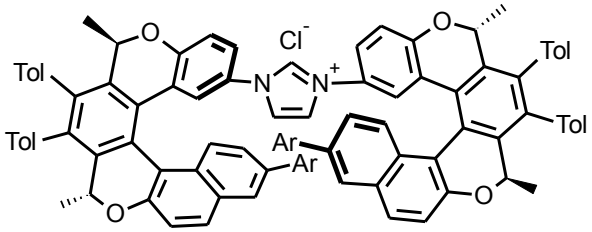
(-)-(*M,R,R*)-**139a**



(-)-(*M,R,R*),(*M,R,R*)-**208**



(-)-(*M,R,R*),(*M,R,R*)-**180a-f**



(-)-(*M,R,R*),(*M,R,R*)-**207**

Figure 21 Overview of the synthesised symmetrical and unsymmetrical imidazolium salts

This research has opened up the field of asymmetric catalysis using helicene-based N-heterocyclic carbene ligands in metal catalysed transformations. We believe that these ligands can be used with different metals in other asymmetric transformations. In order to improve the chirality transfer in the enantioselective metal catalysed [2+2+2]

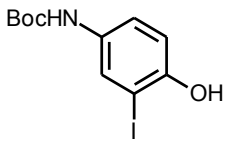
cycloisomerisation, further structural modifications of the helicene units of the respective NHC ligands are required. Since the multi-step mechanism of enantioselective Ni^0-catalysed triyne [2+2+2] cyclotrimerisation to dibenzohelicenes is not known in all details as, namely, the moment of chirality transfer, further mechanistic investigation with the support of molecular modelling at the DFT level is necessary.

5 EXPERIMENTAL SECTION

General: Melting points were determined on Mikro-Heiztisch Polytherm A (Hund, Wetzlar) apparatus and are uncorrected. The NMR spectra were measured on Bruker Avance III HD 400, 500 and 600 instruments, respectively: the ^{1}H NMR spectra at 400.13 MHz, 499.88 MHz and 600.13 MHz, the ^{13}C NMR spectra at 100.61 MHz, 125.71 MHz and 150.90 MHz in $CDCl_3$ or CD_2Cl_2 as indicated in 5 mm PFG probe with indirect detection. For referencing of ^{1}H NMR spectra the residual solvent signals (δ 7.26 for $CHCl_3$ and δ 5.32 for CH_2Cl_2) were used. In the case of ^{13}C spectra the signals of solvents (δ 77.00 for $CDCl_3$ and δ 53.84 for CD_2Cl_2) were used. The chemical shifts are given in δ-scale, the coupling constants *J* are given in Hz. For the assignment of both the ^{1}H and ^{13}C NMR spectra of key compounds, homonuclear 2D-H,H-COSY, 2D-H,H-ROESY and heteronuclear 2D-H,C-HSQC, 2D-H,C-HMBC experiments were performed. The IR spectra were measured in KBr or $CHCl_3$. The EI mass spectra were determined at an ionising voltage of 70 eV, the *m/z* values are given along with their relative intensities (%). The standard 70 eV spectra were recorded in the positive ion mode. The sample was dissolved in chloroform, loaded into a quartz cup of the direct probe and inserted into the ion source. The source temperature was 220 °C. For exact mass measurement, the spectra were internally calibrated using perfluorotri-*n*-butylamine (Heptacosa). The low resolution ESI mass spectra were recorded using a quadrupole orthogonal acceleration time-of-flight tandem mass spectrometer (Q-Tof micro, Waters) and high resolution ESI mass spectra using a hybrid FT mass spectrometer combining a linear ion trap MS and the Orbitrap mass analyser (LTQ Orbitrap XL, Thermo Fisher Scientific). The conditions were optimised for suitable ionisation in the ESI Orbitrap source (sheat gas flow rate 35 a.u., aux gas flow rate 10 a.u. of nitrogen, source voltage 4.3 kV, capillary voltage 40 V, capillary temperature 275 °C, tube lens voltage 155 V). The samples were dissolved in methanol and applied by direct injection. As a mobile phase was used 80% methanol (flow rate 100 μl/min). APCI MS was measured using LTQ Orbitrap XL hybrid FT mass spectrometer equipped with Ion Max source with APCI probe installed (Thermo Fisher Scientific, San Jose, CA, USA) and coupled to Rheos 2200 quaternary gradient pump (Flux Instruments, Reinach, Switzerland; the system was controlled by Xcalibur software (Thermo Fisher Scientific). The APCI vaporizer and heated capillary temperatures were set

to 400 °C and 200 °C, respectively; the corona discharge current was 5 μA. Nitrogen served both as the sheath and auxiliary gas at a flow rate of 55 and 5 arbitrary units, respectively. Samples were dissolved in methanol for both ESI and APCI measurements. Accurate mass measurements were obtained by the EI, APCI or ESI MS. Optical rotations were measured in CH_2Cl_2, $CHCl_3$ or tetrahydrofuran (THF) using an Autopol IV (Rudolph Research Analytical) instrument. The CD spectra were acquired on a J-815 CD spectrometer (Jasco Analytical Instruments, Inc.) in THF (10^{-4} M solutions) using 10 mm quartz sample cell. TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2.4\ H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulphuric acid (10%). The flash chromatography was performed on Silica gel 60 (0.040-0.063 mm, Merck or Fluorochem) or on Biotage® KP-C18-HS SNAP cartridges using Isolera One HPFC system (Biotage, Inc.). Biotage Initiator EXP EU (300 W power) was used for reactions carried out in microwave reactor. *N,N*-Diisopropylamine was distilled from calcium hydride under nitrogen; THF was freshly distilled from sodium/benzophenone under nitrogen; dichloromethane was freshly distilled from calcium hydride; benzene and toluene were freshly distilled from sodium under nitrogen. Otherwise, all commercially available solvents, catalysts and reagent grade materials were used as received. CpCo(CO)(fum) (fum = dimethyl fumarate) was synthesised according to the literature procedure.[147]. The starting materials **141**, **183**, **195**, **209**, **210**, **211**, and **212** were purchased, the materials (–)-(*S*)-**144**,[146] (+)-(*R*)-**145**,[60] **152**,[76] **158**,[151] **168**,[63] (+)-(*R*)-**175**,[164] **213**,[167] **214**[168] and **215**[169] were synthesised according to the literature.

***tert*-Butyl (4-hydroxy-3-iodophenyl)carbamate 147**



4-Amino-2-iodophenol **143** (3.31 g, 14.1 mmol) was dissolved in methanol (30 ml) and triethylamine (4.00 ml, 28.7 mmol, 2.0 equiv.) was added at room temperature. Then di-*tert*-butyl dicarbonate (3.56 ml, 15.5 mmol, 1.1 equiv.) was slowly added and the solution was stirred at room temperature for 3 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 4:1) to afford carbamate **147** (4.55 g, 96%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.79 (bs, 1H), 7.10 (dd, *J* = 8.8, 2.6, 1H), 6.87 (dd, *J* = 8.8, 0.8, 1H), 6.38 (bs, 1H), 5.38 (bs, 1H), 1.50 (s, 9H).

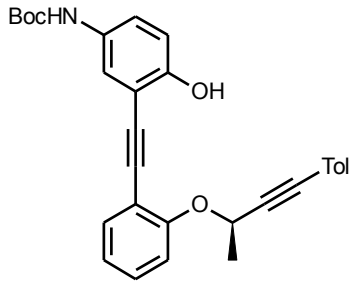
^{13}C NMR (101 MHz, $CDCl_3$): 153.00, 151.12, 132.08, 128.73, 121.39, 114.72, 85.21, 80.75, 28.30.

IR ($CHCl_3$): 3586 w, 3504 m, 3439 m, 3354 w, br, 3091 vw, 2982 m, 2872 w, 2029 w, 1723 s, 1713 s, 1606 w, 1588 m, 1511 vs, 1491 s, 1455 m, 1402 s, 1394 s, 1369 s, 1272 m, 1243 s, sh, 1229 s, 1180 s, sh, 1158 vs, 1124 w, sh, 1056 m, 943 vw, 916 w, 875 w, 815 w, 697 w, 684 w, sh, 567 w, 531 w, 490 w, 461 vw, 446 w cm^{-1}.

ESI MS: 358 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{11}H_{14}O_3NINa$ 357.9911, found 357.9910.

(–)-*tert*-Butyl {4-hydroxy-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]-oxy}phe-nyl)ethynyl]phenyl}carbamate 148



A Schlenk flask was charged with carbamate **147** (400 mg, 1.19 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, 0.024 mmol, 2 mol%), CuI (9 mg, 0.05 mmol, 4 mol%) and purged with argon. Then degassed toluene (7 ml) and *N,N*-diisopropylamine (340 µl, 2.43 mmol, 2.0 equiv.) were added. Then alkyne (+)-(*R*)-**145**[60] (397 mg, 1.53 mmol, 1.3 equiv.) in degassed toluene (5 ml) was added dropwise via cannula to a reaction mixture and the reaction was stirred at room temperature for 3 h. The solvent was evaporated *in vacuo* and the residue was flash

chromatographed on silica gel (hexane-ethyl acetate 10:1) to afford phenol carbamate (–)-(*R*)-**148** (475 mg, 85%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -245° (c 0.071, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (bs, 1H), 7.46 (dd, *J* = 7.5, 1.7, 1H), 7.34 (ddd, *J* = 8.4, 7.5, 1.7, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.17 (dd, *J* = 8.8, 2.7, 1H), 7.10 – 7.07 (m, 2H), 6.99 (td, *J* = 7.5, 1.1, 1H), 6.92 (d, *J* = 8.8, 1H), 6.48 (s, 1H), 6.32 (s, 1H), 5.18 (q, *J* = 6.5, 1H), 2.32 (s, 3H), 1.86 (d, *J* = 6.5, 3H), 1.52 (s, 9H).

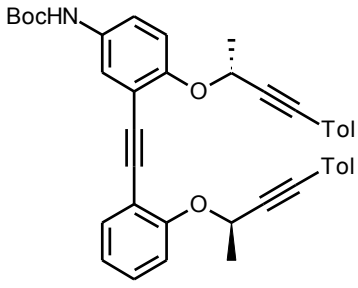
^{13}C NMR (101 MHz, $CDCl_3$): 157.80, 153.54, 153.03, 138.75, 131.86, 131.63, 130.69, 129.77, 128.97, 121.65, 121.18, 120.62, 119.06, 114.61, 113.38, 112.46, 110.06, 93.62, 88.22, 86.76, 86.60, 80.41, 65.29, 28.35, 22.35, 21.46.

IR (KBr): 3446 m, 3056 w, 3030 w, 2870 w, 1724 m, 1702 m, 1594 m, 1392 w, 1368 m, 1280 w , 1162 s, 1122 m, 1020 w, 817 m, 751 m cm^{-1}.

ESI MS: 490 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{30}H_{29}O_4NNa$ 490.1989, found 490.1988.

(–)-*tert*-Butyl (4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)ethynyl]phenyl)carbamate 149



To a solution of (–)-(*R*)-**148** (350 mg, 0.749 mmol), (–)-(S)-**144**[146] (144 mg, 0.899 mmol, 1.2 equiv.), triphenylphosphine (236 mg, 0.899 mmol, 1.2 equiv.) in dry benzene (5 ml), diisopropyl azodicarboxylate (177 µl, 0.899 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 4 h, the solvent was evaporated *in vacuo* and the crude mixture was purified by flash chromatography on silica gel (hexane-diethyl ether 40:1) to afford the desired triyne (–)-(*R,R*)-**149** (411 mg, 90%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -109° (c 0.450, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.52 (dd, *J* = 7.6, 1.7, 1H), 7.44 (d, *J* = 2.7, 1H), 7.36 (bd, *J* = 7.7, 1H), 7.31 – 7.26 (m, 5H), 7.20 (dd, *J* = 8.3, 1.1, 1H), 7.15 (d, *J* = 8.9, 1H), 7.10 – 7.06 (m, 4H), 6.98 (td, *J* = 7.5, 1.2, 1H), 6.34 (s, 1H), 5.20 (q, *J* = 6.5, 1H), 5.19 (q, *J* = 6.5, 1H), 2.32 (s, 6H), 1.82 (d, *J* = 6.5, 3H), 1.80 (d, *J* = 6.5, 3H), 1.52 (s, 9H).

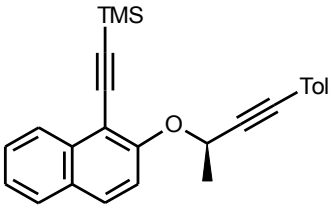
^{13}C NMR (101 MHz, $CDCl_3$): 158.16, 154.13, 152.85, 138.49, 138.44, 133.59, 132.60, 131.58 (2C), 129.34, 128.94, 128.92, 123.61, 121.59, 119.99, 119.43, 119.42, 117.87, 115.94, 115.63, 114.53, 90.28, 89.65, 87.78, 87.66, 86.05 (2C), 80.47, 66.99, 66.09, 28.33, 22.49, 22.47, 21.45 (2C).

IR (KBr): 3404 w, 3337 w, br, 3080 vw, sh, 3053 vw, 3028 w, 2982 m, 2924 m, 2233 w, 2206 vw, sh, 1726 s, 1701 s, br, 1609 m, 1594 m, 1585 m, sh, 1574 m, 1520 s, sh, 1508 vs, 1498 vs, 1486 s, 1447 s, 1412 m, 1392 m, 1367 s, 1328 s, 1260 s, 1242 s, 1159 vs, 1123 s, 1106 m, sh, 1084 s, 1033 s, 1019 s, 943 m, 923 m, sh, 834 w, 816 s, 749 s, 709 w, 663 vw, 646 vw, 537 w cm^{-1}.

ESI MS: 632 ($[M+Na]^+$).

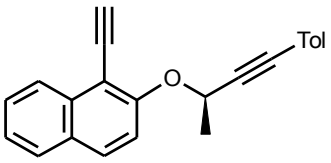
HR ESI MS: calcd for $C_{41}H_{39}O_4NNa$ 632.2771, found 632.2772.

(+)-Trimethyl[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naphthalen-1-yl)ethy-nyl]silane 153



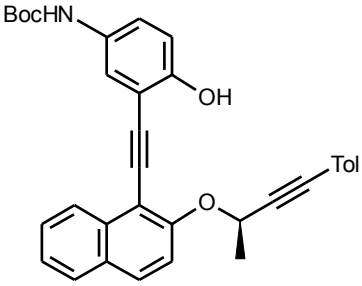
To a solution of naphthol **152**[76] (340 mg, 1.41 mmol), (–)-(*S*)-**144**[146] (276 mg, 1.73 mmol, 1.2 equiv.), triphenylphosphine (445 mg, 1.70 mmol, 1.2 equiv.) in benzene (6 ml), diisopropyl azodicarboxylate (340 µl, 1.72 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 2.5 h, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 50:1) to afford the protected diyne (+)-(*R*)-**153** (496 mg, 92%) as a colourless oil. NMR spectra were in agreement with the published data.[170]

(–)-1-Ethynyl-2-{[(2*R*)-4-(4-methylphenyl)but-3-yn-2-yl]oxy}naphthalene 154



To a solution of the protected diyne (+)-(*R*)-**153** (496 mg, 1.30 mmol) in methanol (7 ml), anhydrous potassium carbonate (358 mg, 2.60 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred at room temperature for 3 h. Then it was diluted with a saturated ammonium chloride solution (20 ml), extracted with diethyl ether (3 x 15 ml) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (hexane-diethyl ether 50:1) to give diyne (–)-(*R*)-**154** (394 mg, 98%) as a colourless oil. NMR spectra were in agreement with the published data.[170]

(–)-*tert*-Butyl{4-hydroxy-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naph-thalen-1-yl)ethynyl]phenyl}carbamate 155



A Schlenk flask was charged with iodide **147** (355 mg, 1.06 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg, 0.021 mmol, 2 mol%) and CuI (10 mg, 0.053 mmol, 5 mol%) and purged with argon. Then degassed benzene (4 ml) and *N,N*-diisopropylamine (300 µl, 2.14 mmol, 2.0 equiv.) were added and the mixture was heated at 45 °C. Then alkyne (–)-(*R*)-**154** (392 mg, 1.26 mmol, 1.2 equiv.) in degassed benzene (5 ml) was added dropwise to the reaction mixture and the reaction was stirred at 45 °C for 4.5 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane-ethyl acetate 20:1) to afford phenol carbamate (–)-(*R*)-**155** (458 mg, 83%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -305° (c 0.277, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 8.34 – 8.30 (m, 1H), 7.85 (d, *J* = 9.1, 1H), 7.83 – 7.80 (m, 1H) 7.68 (bs, 1H), 7.62 – 7.57 (m, 1H), 7.56 (d, *J* = 9.1, 1H), 7.45 – 7.41 (m, 1H), 7.29 – 7.26 (m, 2H), 7.15 (dd, *J* = 8.9, 2.7, 1H), 7.09 – 7.05 (m, 2H), 6.97 (dd, *J* = 8.8, 0.8, 1H), 6.67 (d, *J* = 0.8, 1H), 6.39 (bs, 1H), 5.36 (q, *J* = 6.5, 1H), 2.31 (s, 3H), 1.92 (d, *J* = 6.5, 3H), 1.55 (s, 9H).

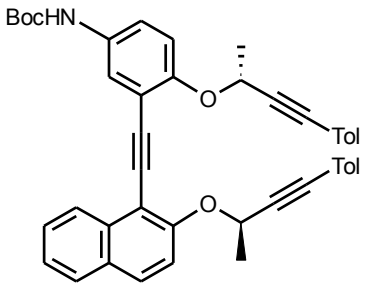
^{13}C NMR (101 MHz, $CDCl_3$): 156.93, 153.41, 153.07, 138.76, 133.29, 131.61, 130.75, 129.97, 128.95, 128.71, 128.03, 127.44, 125.39, 124.66, 121.47, 120.51, 118.96, 114.77, 114.65, 110.40, 106.95, 93.35, 92.11, 86.92, 86.81, 80.41, 66.04, 28.37, 22.47, 21.44.

IR (KBr): 3436 m, br, 3058 vw, 3030 vw, 2980 w, 2870 w, 2244 vw, sh, 2225 vw, 1725 m, sh, 1699 s, 1685 s, 1622 m, 1587 m, 1526 m, sh, 1510 s, 1495 s, sh, 1467 m, 1418 vw, 1392 m, 1369 s, 1329 m, 1285 m, 1268 s, 1247 vs, 1162 vs, 1117 m, 1083 m, 1038 m, 1026 m, sh, 1020 m, sh, 816 s, 708 vw, 666 w cm^{-1}.

ESI MS: 540 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{34}H_{31}O_4NNa$ 540.2145, found 540.2146.

(–)-*tert*-Butyl (4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naphthalen-1-yl)ethynyl]phenyl)-carbamate 151



To a solution of phenol (–)-(*R*)-**155** (410 mg, 0.793 mmol), (–)-(*S*)-**144**[146] (152 mg, 0.949 mmol, 1.2 equiv.), triphenylphosphine (249 mg, 0.950 mmol, 1.2 equiv.) in benzene (5 ml), diisopropyl azodicarboxylate (190 µl, 0.965 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was left stirring at room temperature for 2.5 h, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 50:1) to afford triyne (–)-(*R,R*)-**151** (460 mg, 88%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -110° (c 0.526, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 8.60 (bd, *J* = 8.4, 1H), 7.82 – 7.78 (m, 2H), 7.55 (ddd, *J* = 8.3, 6.8, 1.3, 1H), 7.50 (d, *J* = 9.0, 2H), 7.43 (bd, *J* = 2.7, 1H), 7.41 (ddd, *J* = 8.1, 6.9, 1.3, 1H), 7.30 – 7.26 (m, 4H), 7.21 (d, *J* = 9.0, 1H), 7.09 – 7.05 (m, 4H), 6.35 (bs, 1H), 5.41 (q, *J* = 6.5, 1H), 5.24 (q, *J* = 6.5, 1H), 2.32 (s, 6H), 1.89 (d, *J* = 6.5, 3H), 1.88 (d, *J* = 6.5, 3H), 1.53 (s, 9H).

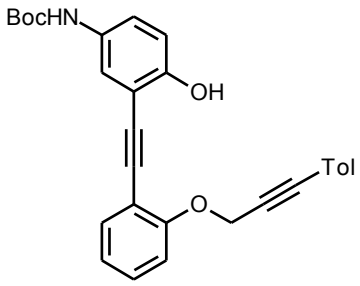
^{13}C NMR (101 MHz, $CDCl_3$): 157.19, 154.22, 152.90, 138.50 (2C), 134.57, 132.23, 131.61, 131.56, 129.51, 129.42, 128.96, 128.93, 127.88, 126.96, 126.12, 124.68, 123.40, 120.23, 119.40, 119.33, 118.30, 116.21, 115.13, 109.87, 95.39, 88.46, 87.94, 87.61, 86.19 (2C), 80.46, 67.52, 66.22, 28.35, 22.64, 22.58, 21.44 (2C).

IR (KBr): 3410 m, 3342 w, br, 3055 w, 2983 m, 2231 w, 1725 s, 1707 m, 1700 m, 1622 w, sh, 1609 m, 1588 m, 1570 vw, 1523 s, br, sh, 1510 vs, 1498 vs, 1466 m, 1434 w, 1392 w, 1368 m, 1328 m, 1282 m, sh, 1268 s, 1246 s, 1158 vs, 1125 s, 1084 s, 1038 s, 1030 m, sh, 1019 m, 944 w, 816 s, 667 w, 536 vw cm^{-1}.

ESI MS: 682 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{45}H_{41}O_4NNa$ 682.2928, found 682.2929.

tert-Butyl {4-hydroxy-3-[(2-{[3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)ethynyl]-phenyl}carbamate 169



A Schlenk flask was charged with iodide **147** (320 mg, 0.955 mmol), $PdCl_2(PPh_3)_2$ (26 mg, 0.037 mmol, 4 mol%) and CuI (14 mg, 0.074 mmol, 8 mol%) and purged with argon. Then degassed toluene (8 ml) and *N,N*-diisopropylamine (160 µl, 1.14 mmol, 1.2 equiv.) were added. Then alkyne **168**[63] (280 mg, 1.14 mmol, 1.2 equiv.) in degassed toluene (3 ml) was added *via* canula to the reaction mixture and the reaction was stirred for 16 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane–ethyl acetate 8:1) to afford phenol carmabate **169** (420 mg, 99%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.47 (bdd, J = 7.6, 1.7, 2H), 7.38 – 7.33 (m, 3H), 7.18 (dd, J = 8.8, 2.7, 1H), 7.15 – 7.10 (m, 3H), 7.01 (td, J = 7.5, 0.9 1H), 6.91 (d, J = 8.8, 1H), 6.60 (bs, 1H), 6.34 (s, 1H), 5.04 (s, 2H), 2.34 (s, 3H), 1.52 (s, 9H).

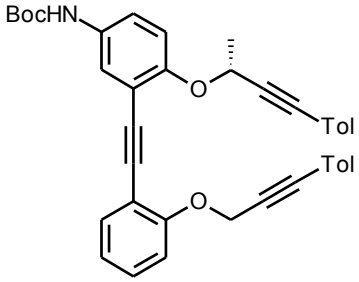
^{13}C NMR (101 MHz, $CDCl_3$): 157.93, 153.61, 138.92, 131.86, 131.72, 130.68, 129.83, 129.01, 121.70, 121.39, 120.60, 119.01, 114.74, 112.38, 112.08, 109.97, 93.25, 88.72, 88.27, 82.33, 80.40, 57.46, 28.35, 21.49. Carbamate carbon was not found.

IR ($CHCl_3$): 3470 w, br, 3441 m, 2982 w, 2242 vw, 2213 vw, 1724 vs, 1610 vw, sh, 1597 w, 1591 w, 1575 w, 1511 s, 1497 s, 1489 s, 1450 w, sh, 1427 m, 1417 m, 1393 w, 1369 m, 1280 m, 1244 s, 1160 vs, 1118 w, 1023 m, 819 m cm^{-1}.

ESI MS: 476 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{29}H_{27}O_4NNa$ 476.1832, found 476.1833.

(+)-*tert*-Butyl (4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-3-[(2-{[3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)ethynyl]phenyl)carbamate 164



To a solution of **169** (405 mg, 0.893 mmol), (–)-(S)-**144**[146] (164 mg, 1.02 mmol, 1.2 equiv.), triphenylphosphine (270 mg, 1.03 mmol, 1.2 equiv.) in dry benzene (12 ml), diisopropyl azodicarboxylate (200 µl, 1.02 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 16 h, methanol (5 ml) was added and the solvent were evaporated *in vacuo*. The residue was flash chromatographed on silica gel (hexane–ethyl acetate 20:1) to afford the desired triyne (+)-(*R*)-**164** (467 mg, 89%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D = +24.0°$ (c 0.533, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 7.53 (dd, *J* = 7.6, 1.7, 1H), 7.495 (bs, 1H), 7.33 (bs, 1H), 7.31 (ddd, *J* = 8.4, 7.5, 1.7, 1H), 7.31 (m, 2H), 7.27 (m, 2H), 7.16 (d, *J* = 8.9, 1H), 7.15 (dd, *J* = 8.4, 1.1, 1H), 7.10 – 7.06 (m, 4H), 6.98 (td, *J* = 7.5, 1.1, 1H), 6.34 (s, 1H), 5.20 (q, *J* = 6.6, 1H), 5.05 (s, 2H), 2.32 (s, 6H), 1.80 (d, *J* = 6.6, 3H), 1.51 (s, 9H).

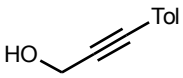
^{13}C NMR (151 MHz, $CDCl_3$): 158.27, 154.25, 152.85, 138.72, 138.43, 133.69, 132.66, 131.68, 131.59, 129.43, 129.00, 128.93, 123.38, 121.40, 119.91, 119.46, 119.28, 118.08, 115.62, 113.78, 113.68, 90.12, 89.79, 87.84, 87.58, 86.08, 83.30, 80.46, 67.08, 57.65, 28.34, 22.40, 21.47, 21.45.

IR ($CHCl_3$): 3440 w, 2983 w, 2236 w, 2215 vw, 1724 s, 1609 w, 1596 w, 1583 w, 1575 w, 1518 s, 1510 vs, 1500 vs, 1489 s, 1454 m, 1413 m, 1394 m, 1369 m, 1328 w, 1279 m, 1238 s, 1158 vs, 1124 m, 1120 w, 1106 w, 1049 w, 1023 m, 1020 m, 819 s, 536 w cm^{-1}.

ESI MS: 618 ([M+Na]$^+$).

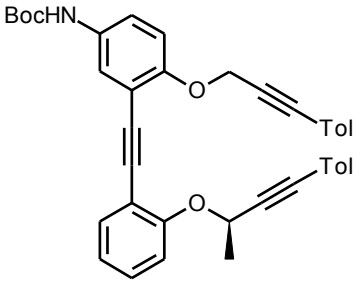
HR ESI MS: calcd for $C_{40}H_{37}O_4NNa$ 618.2615, found 618.2615.

3-(4-Methylphenyl)prop-2-yn-1-ol 171



A Schlenk flask was charged with 1-iodo-4-methylbenzene (5.00 g, 22.9 mmol), $Pd(PPh_3)_4$ (141 mg, 0.122 mmol, 5 mol%) and CuI (43 mg, 0.23 mmol, 10 mol%) and purged with argon. Then degassed toluene (31 ml) and *N,N*-diisopropylamine (12.5 ml, 89.2 mmol, 3.4 equiv.) were added. Then 2-propyn-1-ol (1.60 ml, 27.5 mmol, 1.2 equiv.) was added to the reaction mixture and the reaction was stirred for 2.5 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane–ethyl acetate 10:1) to afford alcohol **171** (3.13 g, 93%) as an orange oil. NMR spectra were in agreement with the published data.[163]

(–)-*tert*-Butyl(3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)-ethynyl]-4-{[3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)carbamate 165



To a solution of (–)-(*R*)-**148** (400 mg, 0.855 mmol), **171** (184 mg, 1.26 mmol, 1.5 equiv.), triphenylphosphine (344 mg, 1.31 mmol, 1.5 equiv.) in dry benzene (10 ml), diisopropyl azodicarboxylate (250 µl, 1.27 mmol, 1.5 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 16 h, the solvent was evaporated *in vacuo* and the crude mixture was purified by flash chromatography on silica gel (hexane-diethyl ether 40:1) and then on C-18 reversed-phase silica gel (methanol) to afford the desired triyne (–)-(*R*)-**165** (422 mg, 83%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -119° (c 0.293, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 7.53 (dd, *J* = 7.6, 1.7, 1H), 7.46 (d, *J* = 2.4, 1H), 7.37 (bd, *J* = 8.8, 1H), 7.30 (m, 2H), 7.285 (ddd, *J* = 8.2, 7.5, 1.7, 1H), 7.27 (m, 2H), 7.21 (dd, *J* = 8.2, 1.1, 1H), 7.09 (d, *J* = 8.8, 1H), 7.08 (m, 4H), 6.98 (td, *J* = 7.6, 1.1, 1H), 6.34 (s, 1H), 5.21 (q, *J* = 6.5, 1H), 5.03 (s, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 1.83 (d, *J* = 6.5, 3H), 1.52 (s, 9H).

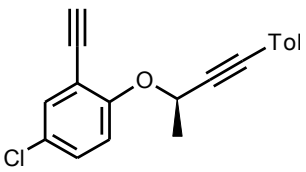
^{13}C NMR (151 MHz, $CDCl_3$): 158.30, 154.32, 152.88, 138.68, 138.48, 133.45, 132.34, 131.68, 131.59, 129.40, 128.98, 128.95, 123.82, 121.62, 120.07, 119.44, 119.30, 116.04, 115.33, 114.67, 114.46, 90.45, 89.47, 87.69, 87.57, 86.09, 83.44, 80.49, 66.16, 58.43, 28.34, 22.44, 21.46, 21.45.

IR ($CHCl_3$): 3440 w, 2983 w, 2236 w, 2216 vw, 1724 s, 1610 w, 1595 w, 1585 w, 1574 w, 1519 s, 1510 vs, 1501 vs, 1487 s, 1448 m, 1414 w, 1394 m, 1369 m, 1279 m, 1241 s, 1158 vs, 1124 w, 1119 w, 1023 m, 819 s cm^{-1}.

ESI MS: 618 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{40}H_{37}O_4NNa$ 618.2615, found 618.2615.

(+)-4-Chloro-2-ethynyl-1-{[(2*R*)-4-(4-methylphenyl)but-3-yn-2-yl]oxy}benzene 176



To a solution of the protected diyne (+)-(*R*)-**175**[164] (546 mg, 1.49 mmol) in methanol (10 ml), anhydrous potassium carbonate (416 mg, 3.01 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred at room temperature for 2 h. Then a saturated ammonium chloride solution (20 ml) was added, the solution was extracted with diethyl ether (3 x 30 ml) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 50:1) to give diyne (+)-(*R*)-**176** (407 mg, 93%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D = +44°$ (c 0.361, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.43 (bd, J = 2.6, 1H), 7.29 – 7.25 (m, 3H), 7.13 (d, J = 8.9, 1H), 7.11 – 7.09 (m, 2H), 5.08 (q, J = 6.6, 1H), 3.31 (s, 1H), 2.34 (s, 3H), 1.78 (d, J = 6.6, 3H).

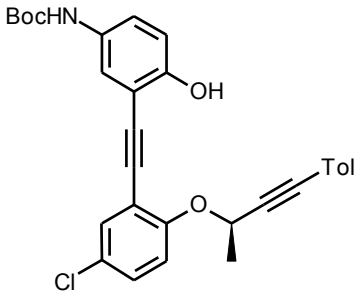
^{13}C NMR (101 MHz, $CDCl_3$): 157.51, 138.81, 133.44, 131.57, 129.78, 129.02, 126.06, 119.04, 116.28, 114.29, 86.74, 86.62, 82.32, 78.67, 66.12, 22.26, 21.47.

IR ($CHCl_3$): 3306 m, 3083 vw, 3054 vw, 2236 w, 2111 vw, 1607 vw, 1593 w, 1570 vw, 1511 s, 1484 vs, 1462 m, 1409 vw, sh, 1395 m, 1376 w, 1331 m, 1267 vw, sh, 1247 s, 1181 m, 1133 s, 1121 w, 1108 w, 1084 m, 1036 m, 1020 w, 885 w, 819 s, 809 m, 709 vw, 659 m, 621 m, 545 w, 478 vw cm^{-1}.

APCI MS: 295 ($[M+H]^+$).

HR APCI MS: calcd for $C_{19}H_{16}O^{35}Cl$ 295.0884, found 295.0889.

(–)-*tert*-Butyl {3-[(5-chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)-ethynyl]-4-hydroxyphenyl}carbamate 177



A Schlenk flask was charged with iodide **147** (613 mg, 1.83 mmol), $Pd(PPh_3)_2Cl_2$ (30 mg, 0.043 mmol, 2 mol%), CuI (14 mg, 0.074 mmol, 4 mol%) and purged with argon. Then degassed toluene (30 ml) and *N,N*-diisopropylamine (300 µl, 2.14 mmol, 1.2 equiv.) were added. Then alkyne (+)-(*R*)-**176** (648 mg, 2.20 mmol, 1.2 equiv.) in degassed toluene (5 ml) was added dropwise to a reaction mixture via cannula and the reaction was stirred at room temperature for 3 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane-ethyl acetate 10:1) to afford phenol carbamate (–)-(*R*)-**177** (743 mg, 81%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -227° (c 0.288, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.46 (bs, 1H), 7.42 (d, *J* = 2.6, 1H), 7.29 – 7.27 (m, 3H), 7.20 (dd, *J* = 8.8, 2.6, 1H), 7.16 (d, *J* = 8.9, 1H), 7.10 – 7.08 (m, 2H), 6.92 (d, *J* = 8.8, 1H), 6.37 (bs, 1H), 6.33 (bs, 1H), 5.14 (q, *J* = 6.6, 1H), 2.33 (s, 3H), 1.85 (d, *J* = 6.6, 3H), 1.52 (s, 9H).

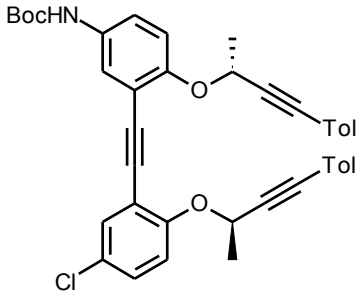
^{13}C NMR (101 MHz, $CDCl_3$): 156.37, 153.64, 153.01, 138.94, 131.63, 131.21, 130.81, 129.46, 129.02, 126.05, 122.04, 120.79, 118.82, 114.78, 114.62, 114.09, 109.52, 92.20, 89.34, 87.02, 86.25, 80.49, 65.74, 28.35, 22.28, 21.48.

IR ($CHCl_3$): 3442 m, 2983 m, 2872 w, 2236 w, 2216 vw, 1723 s, 1624 w, 1610 m, 1589 w, 1567 w, 1522 s, 1511 s, 1496 s, 1431 m, 1418 m, 1394 m, 1369 m, 1331 m, 1285 m, 1250 m, 1159 vs, 1121 m, 1086 m, 1055 m, 1020 m, 988 vw, 819 m, 808 m, 542 w cm^{-1}.

ESI MS: 524 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{30}H_{28}O_4N^{35}ClNa$ 524.1599, found 524.1600.

(–)-*tert*-Butyl (3-[(5-chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-phenyl)-ethynyl]-4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)-carbamate 178



To a solution of phenol (–)-(*R*)-**177** (380 mg, 0.758 mmol), (–)-(*S*)-**144**[146] (145 mg, 0.905 mmol, 1.2 equiv.), triphenylphosphine (236 mg, 0.901 mmol, 1.2 equiv.) in benzene (5 ml), diisopropyl azodicarboxylate (180 µl, 0.914 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 3 h, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 40:1) to afford triyne (–)-(*R,R*)-**178** (376 mg, 77%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_{D}$ = -119° (c 0.294, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.48 (d, *J* = 2.6, 1H), 7.45 (bd, *J* = 2.7, 1H), 7.36 (bd, *J* = 8.1, 1H), 7.28 – 7.25 (m, 4H), 7.23 (dd, *J* = 8.8, 2.6, 1H), 7.16 – 7.12 (m, 2H), 7.10 – 7.06 (m, 4H), 6.34 (bs, 1H), 5.16 (q, *J* = 6.5, 1H), 5.15 (q, *J* = 6.5, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 1.81 (d, *J* = 6.5, 3H), 1.79 (d, *J* = 6.5, 3H), 1.52 (s, 9H).

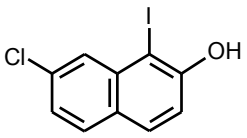
^{13}C NMR (101 MHz, $CDCl_3$): 156.76, 154.23, 152.83, 138.67, 138.50, 132.88, 132.51, 131.59, 131.58, 129.08, 128.99, 128.94, 126.40, 123.68, 120.41, 119.35, 119.19, 117.42, 117.15, 116.18, 114.94, 90.83, 88.83, 87.60, 87.15, 86.44, 86.16, 80.54, 66.85, 66.45, 28.33, 22.47, 22.43, 21.46, 21.45.

IR ($CHCl_3$): 3440 w, 2985 m, 2871 w, 2235 w, 2217 vw, 1724 s, 1609 m, 1585 w, 1567 w, 1517 s, 1510 s, 1499 s, 1421 m, 1392 m, 1369 m, 1330 m, 1281 m, 1246 m, 1159 vs, 1086 m, 1056 w, 1020 m, 819 m, 708 vw, 541 w cm^{-1}.

ESI MS: 666 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{41}H_{38}O_4N^{35}ClNa$ 666.2382, found 666.2383.

7-Chloro-1-iodonaphthalen-2-ol 184



Naphthol **183** (1.0 g, 5.6 mmol) and sodium carbonate (1.23 g, 11.6 mmol, 2.0 equiv.) were dissolved in a mixture of tetrahydrofuran (20 ml) and water (5 ml). Then iodine (1.39 g, 5.48 mmol, 1.0 equiv.) was added to the solution. The reaction mixture was stirred at room temperature for 4 h, the reaction was quenched with a saturated solution of ammonium chloride (30 ml) and the saturated solution of sodium thiosulfate (10 ml). The water phase was extracted with dichloromethane (2 x 50 ml) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane–dichloromethane 4:1 to 1:1) to afford chloroiodonaphtol **184** (1.55 g, 91%) as off-white needles.

M.p: 143-144 °C (hexane – dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (dt, J = 1.9, 0.7, 1H), 7.65 – 7.71 (m, 2H), 7.31 (dd, J = 8.7, 2.0, 1H), 7.23 (d, J = 8.9, 1H), 5.81 (s, 1H).

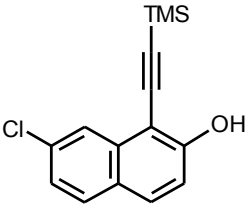
^{13}C NMR (101 MHz, $CDCl_3$): 154.61, 135.79, 134.47, 130.45, 129.90, 129.30, 127.85, 125.07, 116.67, 84.69.

IR ($CHCl_3$): 3584 w, 3480 m, 1619 s, 1502 s, 1420 m, 1374 m, 1353 m, 1264 w, 1183 vs, 1131 m, 1088 m, sh, 954 s, 864 m, 836 s, 649 w, 514 m, 426 w cm^{-1}.

APCI MS: 303 ($[M]^+$).

HR APCI MS: calcd for $C_{10}H_6O^{35}ClI$ 303.9146, found 303.9147.

7-Chloro-1-{[trimethylsilyl]ethynyl}naphthalen-2-ol 185



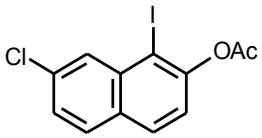
A Schlenk flask was charged with iodide **184** (1.1 g, 3.6 mmol), $PdCl_2(PPh_3)_2$ (51.5 mg, 0.07 mmol, 2 mol%), CuI (29.5 mg, 0.16 mmol, 4 mol%), and purged with argon. Then degassed toluene (38 ml) and *N,N*-diisopropylamine (840 µl, 5.99 mmol, 1.7 equiv.) were added. Then (ethynyltrimethyl)silane (0.9 ml, 6.32 mmol, 1.8 equiv.) in degassed toluene (2 ml) was added dropwise to the reaction mixture and the reaction was

stirred at room temperature for 16 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane – ethyl acetate 6:1) to afford **185** (49 mg, 4%) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (bd, *J* = 2.1, 1H), 7.69 (dd, *J* = 9.0, 8.7, 1H), 7.30 (dd, *J* = 8.6, 2.1, 1H), 7.17 (d, *J* = 8.9, 1H), 6.24 (s, 1H), 0.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): 157.36, 134.33, 133.67, 130.55, 129.72, 126.51, 124.93, 123.88, 116.48, 108.04, 102.30, 96.66, 0.09.

7-Chloro-1-iodonaphthalen-2-yl acetate 186



To a solution of naphthol **184** (1.45 g, 4.77 mmol), triethylamine (1.7 ml, 12 mmol, 2.5 equiv.) in dichloromethane (30 ml), acetylchloride (510 µl, 7.17 mmol, 1.5 equiv.) was added dropwise at 0 °C under argon. The reaction mixture was stirred at room temperature for 5 h. The mixture was quenched with a saturated solution of ammonium chloride (20 ml) and extracted with dichloromethane (2 x 40 ml). The combined organic layers were dried over anhydrous $MgSO_4$, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane–diethyl ether 2:1) to afford the compound **186** (1.61 g, 98%) as an off-white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.19 (dt, *J* = 2.0, 0.6, 1H), 7.81 (d, *J* = 8.7, 1H), 7.75 (d, *J* = 8.6, 1H), 7.44 (dd, *J* = 8.6, 2.0, 1H), 7.22 (d, *J* = 8.7, 1H), 2.45 (s, 3H).

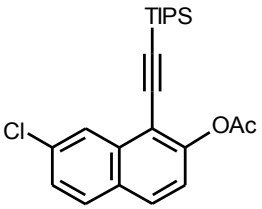
^{13}C NMR (101 MHz, $CDCl_3$): 168.66, 150.95, 136.20, 134.57, 131.04, 130.31, 129.98, 129.95, 127.39, 121.70, 93.19, 21.31.

IR ($CHCl_3$): 3061 vw, 3030 w, 1772 w, sh, 1764 s, 1620 m, 1590 w, sh, 1576 w, sh, 1556 w, 1496 m, 1429 w, 1370 m, 1198 s, sh, 1190 vs, 1088 m cm^{-1}.

EI MS: 346 ($M^{+\bullet}$, 25), 304 (100), 177 (12), 149 (15), 113 (12).

HR EI MS: calcd for $C_{12}H_8O_2{}^{35}ClI$ 345.9258, found 345.9261.

7-Chloro-1-{[tris(1-methylethyl)silyl]ethynyl}naphthalen-2-yl acetate 187



A Schlenk flask was charged with iodide **186** (1.9 g, 5.48 mmol), $PdCl_2(PPh_3)_2$ (82 mg, 0.12 mmol, 2 mol%), CuI (49 mg, 0.26 mmol, 5 mol%), and purged with argon. Then degassed toluene (38 ml) and *N,N*-diisopropylamine (920 µl, 6.56 mmol, 1.2 equiv.) were added and the mixture was heated at 70 °C. Then (triisopropylsilyl)acetylene (1.5 ml, 6.69 mmol, 1.2 equiv.) in degassed toluene (2 ml) was added dropwise to the reaction mixture and the reaction was stirred at 70 °C for 3 h, then at room temperature for another 13 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane–ethyl acetate 4:1) to afford **187** (2.02 g, 92%) as an oil, which solidified in the fridge.

^{1}H NMR (400 MHz, $CDCl_3$): 8.35 (bs, 1H), 7.78 (t, J = 8.8, 2H), 7.44 (dt, J = 8.7, 1.6, 1H), 7.23 (d, J = 8.8, 1H), 2.38 (s, 3H), 1.21 (s, 21H).

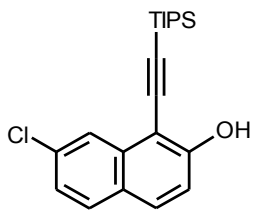
^{13}C NMR (101 MHz, $CDCl_3$): 168.67, 151.39, 135.02, 133.72, 129.65, 129.41, 129.37, 127.11, 125.41, 121.46, 113.00, 102.60, 98.81, 20.96, 18.70, 11.31.

IR ($CHCl_3$): 3059 w, 2866 m, 2149 w, 1783 w, sh, 1762 s, 1617 m, 1601 w, sh, 1588 w, 1505 w, sh, 1497 m, 1471 w, sh, 1463 w, 1384 w, 1364 m, sh, 1369 m, 1093 s, 1064 w, 919 w, 883 m, sh, 880 m, 837 m, 678 m, 664 m, 637 w, sh, 643 w cm^{-1}.

ESI MS: 423 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{23}H_{29}O_2{}^{35}ClNaSi$ 423.1518, found 423.1519.

7-Chloro-1-{[tris(1-methylethyl)silyl]ethynyl}naphthalen-2-ol 188



Acetate **187** (1.99 g, 4.96 mmol) was dissolved in tetrahydrofuran (20 ml) and methanol (20 ml), and potassium carbonate (1.38 g, 9.99 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred at room temperature for 3 h, then it was quenched with a saturated solution of ammonium chloride (50 ml) and extracted with dichloromethane (2 x 50 ml). The combined organic layers were dried over anhydrous

$MgSO_4$. The solvent was evaporated *in vacuo* to afford napthol **188** (1.73 g, 97%) as an oil, which solidified in the fridge.

^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (d, *J* = 2.1, 1H), 7.71 (d, *J* = 8.9, 1H), 7.68 (d, *J* = 8.6, 1H), 7.31 (dd, *J* = 8.6, 2.1, 1H), 7.19 (d, *J* = 8.9, 1H), 6.25 (s, 1H), 1.20 – 1.24 (m, 21H).

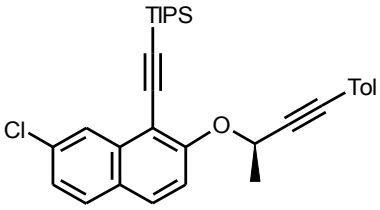
^{13}C NMR (101 MHz, $CDCl_3$): 157.41, 134.46, 133.71, 130.39, 129.73, 126.53, 124.90, 124.01, 116.40, 104.58, 102.66, 98.51, 18.74, 11.23.

IR ($CHCl_3$): 3584 vw, 3497 m, 3059 w, 2959 s, 2945 vs, 2867 vs, 2137 m, 1618 s, 1593 m, 1508 vs, 1462 m, 1446 m, 1435 s, 1384 m, 1371 m, sh, 1361 s, 1342 w, 1195 vs, 1072 w, 996 m, 881 s, 878 s, 837 vs, 679 s, 662 s, 633 m cm^{-1}.

EI MS: 358 ($M^{+\bullet}$, 42), 315 (100), 273 (40), 245 (55), 231 (18), 185 (18), 165 (28), 150 (34), 139 (15), 129 (28), 123 (10), 75 (30), 59 (28).

HR EI MS: calcd for $C_{21}H_{27}O^{35}ClSi$ 358.1520, found 358.1523.

(–)-[(7-Chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naphthalen-1yl)-ethynyl][tris(1-methylethyl)]silane 189



To a solution of naphthol **188** (1.29 g, 3.59 mmol), (–)-(*S*)-**144**[146] (0.632 g, 3.95 mmol, 1.1 equiv.), triphenylphosphine (1.06 g, 4.04 mmol, 1.1 equiv.) in benzene (10 ml) and diisopropylazodicarboxylate (780 µl, 3.96 mmol, 1.1 equiv.) was added dropwise under argon and stirred for 3 h. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane–ethyl acetate 35:1) to afford the protected diyne (–)-(*R*)-**189** (1.41 g, 78%) as a white amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -146° (c 0.270, tetrahydrofuran).

^{1}H NMR (400 MHz, $CDCl_3$): 8.32 (d, *J* = 2.1, 1H), 7.75 (bd, *J* = 9.0, 1H), 7.70 (d, *J* = 8.7, 1H), 7.48 (d, *J* = 9.0, 1H), 7.32 (dd, *J* = 8.7, 2.1, 1H), 7.24 – 7.28 (m, 2H), 7.05 – 7.11 (m, 2H), 5.32 (q, *J* = 6.5, 1H), 2.32 (s, 3H), 1.80 (d, *J* = 6.5, 3H), 1.20 – 1.24 (m, 21H).

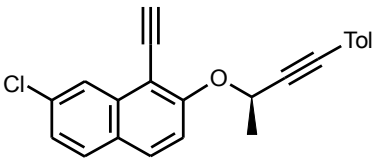
^{13}C NMR (101 MHz, $CDCl_3$): 158.66, 138.66, 135.63, 133.38, 131.55, 129.50, 129.28, 128.97, 127.22, 125.36, 124.73, 119.21, 117.19, 108.45, 101.59, 100.29, 87.46, 86.42, 66.57, 22.53, 21.46, 18.80, 11.45.

IR ($CHCl_3$): 3085 vw, 3056 vw, 2959 s, 2944 s, 2866 vs, 2250 vw, sh, 2228 w, 2147 m, 1615 s, 1588 w, 1572 vw, sh, 1510 s, 1503 s, 1497 s, 1463 m, 1448 m, 1415 vw, sh, 1383 w, 1374 w, 1360 m, 1324 m, 1307 m, 1249 vs, 1180 vw, 1147 m, 1120 m, 1095 vs, 1085 s, 1070 w, sh, 1031 m, sh, 1020 m, 947 vw, 819 s, 865 m, 830 m, 819 s, 621 w, 544 w cm^{-1}.

ESI MS: 501 ($[M+H]^+$).

HR ESI MS: calcd for $C_{32}H_{38}O^{35}ClSi$ 501.2375, found 501.2376.

(–)-7-Chloro-1-ethynyl-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-naphtha-lene 190



To a solution of the protected diyne (–)-(*R*)-**189** (1.04 g, 2.08 mmol) in a mixture of tetrahydrofuran (10 ml) and methanol (0.2 ml) a solution of *n*-tetrabutylammonium fluoride trihydrate (740 mg, 2.35 mmol, 1.1 equiv.) in tetrahydrofuran (10 ml) was added. The reaction mixture was stirred at room temperature for 1 h. Then methanol (20 ml) was added and the mixture was diluted with a saturated solution of ammonium chloride (20 ml), extracted with dichloromethane (3 x 25 ml) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was filtered through a short pad of silica gel (dichloromethane) to give diyne (–)-(*R*)-**190** (690 mg, 96%) as an amorphous white solid.

Optical rotation: $[\alpha]^{20}_D$ = -92° (c 0.388, tetrahydrofuran).

^{1}H NMR (400 MHz, $CDCl_3$): 8.28 (dt, *J* = 2.1, 0.7, 1H), 7.79 (bd, *J* = 9.1, 1H), 7.72 (bd, *J* = 8.7, 1H), 7.50 (d, *J* = 9.1, 1H), 7.34 (dd, *J* = 8.7, 2.1, 1H), 7.24 – 7.28 (m, 2H), 7.06 – 7.10 (m, 2H), 5.29 (q, *J* = 6.5, 1H), 3.74 (s, 1H), 2.32 (s, 3H), 1.85 (d, *J* = 6.5, 3H).

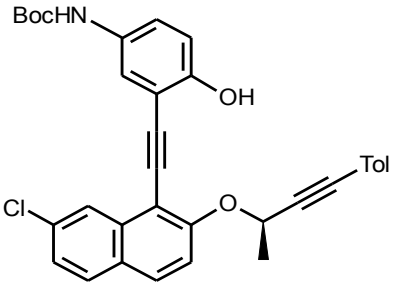
^{13}C NMR (101 MHz, $CDCl_3$): 158.94, 138.75, 135.61, 133.64, 131.56, 129.92, 129.57, 128.99, 127.15, 125.53, 124.33, 119.11, 116.76, 106.70, 87.18, 87.14 (2C), 86.60, 66.72, 22.47, 21.46.

IR ($CHCl_3$): 3305 m, 3084 vw, 3057 w, 2870 w, 2250 vw, sh, 2228 w, 2101 vw, 1617 s, 1588 m, 1573 w, 1510 s, 1504 s, 1497 s, 1448 m, 1420 w, 1408 vw, sh, 1375 w, 1361 m, 1329 m, 1322 m, 1308 m, 1248 vs, 1182 w, 1147 m, 1120 m, 1089 vs, 1085 s, sh, 1066 m, 1032 m, sh, 1020 m, 947 vw, 866 m, 830 s, 658 m, 628 vw, 609 m, 557 w, 438 w cm^{-1}.

ESI MS: 367 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{23}H_{17}O^{35}ClNa$ 367.0860, found 367.0862.

(–)-*tert*-Butyl {3-[(7-chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]-oxy}naphthalen-1-yl)ethynyl]-4-hydroxyphenyl}carbamate 191



A Schlenk flask was charged with iodide **147** (239 mg, 0.713 mmol), $PdCl_2(PPh_3)_2$ (11 mg, 0.016 mmol, 2 mol%) and CuI (5 mg, 0.03 mmol, 4 mol%) and purged with argon. Then degassed toluene (15 ml) and *N,N*-diisopropylamine (120 µl, 0.856 mmol, 1.2 equiv.) were added and the mixture was heated at 40 °C. Then alkyne (–)-(*R*)-**190** (297 mg, 0.861 mmol, 1.2 equiv.) in degassed toluene (7 ml) was slowly added *via* cannula to the reaction mixture and the reaction was stirred at 40 °C for 3.5 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane–ethyl acetate 20:1 to 10:1) to afford phenol carmabate (–)-(*R*)-**191** (296 mg, 75%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -367° (c 0.291, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 8.26 (dt, *J* = 2.0, 0.7, 1H), 7.81 (dt, *J* = 9.0, 0.7, 1H), 7.73 (dt, *J* = 8.6, 0.7, 1H), 7.61 (bs, 1H), 7.55 (d, *J* = 9.0, 1H), 7.35 (dd, *J* = 8.6, 2.0, 1H), 7.27 (m, 2H), 7.22 (bd, *J* = 8.7, 1H), 7.07 (m, 2H), 6.96, (d, *J* = 8.7, 1H), 6.61 (s, 1H), 6.37 (bs, 1H), 5.35 (q, *J* = 6.5, 1H), 2.31 (s, 3H), 1.92 (d, *J* = 6.5, 3H), 1.54 (s, 9H).

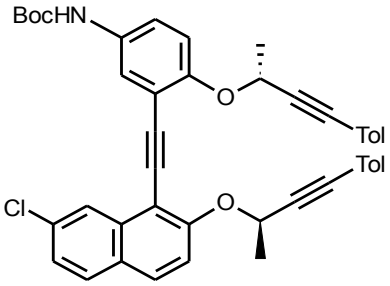
^{13}C NMR (151 MHz, $CDCl_3$): 157.62, 153.53, 153.10, 138.89, 134.09, 133.79, 131.63, 130.80, 129.76, 129.62, 129.00, 126.90, 125.66, 124.22, 121.91, 120.62, 118.85, 114.79, 114.75, 110.09, 106.29, 93.85, 91.41, 87.03, 86.63, 80.44, 66.11, 28.37, 22.44, 21.46.

IR ($CHCl_3$): 3441 m, 2983 w, 2869 w, sh, 2250 w, 2228 w, 1723 s, 1618 m, 1589 w, 1568 w, 1520 s, 1510 vs, 1502 vs, 1438 m, 1411 m, 1393 w, 1369 m, 1330 m, 1285 m, 1250 s, 1183 m, sh, 1158 vs, 1083 s, 1059 m, 1038 m, 1028 m, sh, 819 s, 813 m, 708 w, 544 w cm^{-1}.

ESI MS: 574 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{34}H_{30}O_4N^{35}ClNa$ 574.1756, found 574.1756.

(–)-*tert*-Butyl(3-[(7-chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]-oxy}naphthalen-1-yl)ethynyl]-4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]-oxy}phenyl)carbamate 192



To a solution of phenol (–)-(*R*)-**191** (282 mg, 0.511 mmol), (–)-(*S*)-**144**[146] (96 mg, 0.60 mmol, 1.2 equiv.), triphenylphosphine (160 mg, 0.611 mmol, 1.2 equiv.) in benzene (10 ml) and diisopropyl azodicarboxylate (120 µl, 0.610 mmol, 1.2 equiv.) was added dropwise under argon to the yellow suspension. The reaction mixture was left stirring at room temperature for 3 h, methanol was added (5 ml) and the solvents were evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane–ethyl acetate 50:1) to afford triyne (–)-(*R,R*)-**192** (256 mg, 72%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -174° (c 0.695, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 8.52 (bd, *J* = 2.0, 1H), 7.76 (bd, *J* = 8.9, 1H), 7.72 (d, *J* = 8.7, 1H), 7.50 (bs, 1H), 7.49 (d, *J* = 9.0, 1H), 7.44 (d, *J* = 2.7, 1H), 7.35 (dd, *J* = 8.7, 2.1, 1H), 7.29 – 7.26 (m, 4H), 7.23 (d, *J* = 9.0, 1H), 7.09 – 7.05 (m, 4H), 6.35 (bs, 1H), 5.38 (q, *J* = 6.5, 1H), 5.21 (q, *J* = 6.5, 1H), 2.31 (s, 6H), 1.92 (d, *J* = 6.5, 3H), 1.89 (d, *J* = 6.5, 3H), 1.53 (s, 9H).

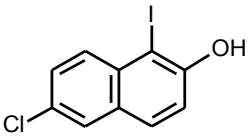
^{13}C NMR (101 MHz, $CDCl_3$): 157.91, 154.28, 152.90, 138.60, 138.45, 135.34, 133.37, 132.13, 131.60, 131.55, 129.49, 129.25, 128.98, 128.90, 127.51, 125.60, 124.80, 123.49, 120.51, 119.36, 119.26, 117.92, 116.00, 114.72, 109.01, 95.82, 87.63, 87.61, 87.60, 86.39, 86.22, 80.46, 67.22, 66.24, 28.34, 22.68, 22.60, 21.44, 21.43.

IR ($CHCl_3$): 3440 w, 2985 w, 2869 w, 2230 w, 1723 m, 1614 m, 1587 w, 1565 w, 1520 m, sh, 1519 m, sh, 1510 s, 1498 vs, 1430 w, 1406 w, sh, 1394 m, 1369 m, 1326 m, 1275 m, 1254 m, 1185 w, sh, 1157 vs, 1106 w, 1028 m, 1020 m, 819 w, 709 w, 664 w cm^{-1}.

ESI MS: 716 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{45}H_{40}O_4N^{35}ClNa$ 716.2538, found 716.2541.

6-Chloro-1-iodonaphthalen-2-ol 196



Naphthol **195** (600 mg, 3.36 mmol) and sodium carbonate (714 mg, 6.74 mmol, 2.0 equiv.) were dissolved in a mixture of tetrahydrofuran (20 ml) and water (5 ml). Then iodine (865 mg, 3.41 mmol, 1.0 equiv.) was added to the solution. The reaction mixture was stirred at room temperature for 5 h, the reaction was quenched with a saturated solution of ammonium chloride (30 ml) and the saturated solution of sodium thiosulfate (10 ml). The water phase was extracted with dichloromethane (2 x 50 ml) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane–ethyl acetate 4:1) to afford chloroiodonaphtol **196** (980 g, 96%) as off-white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (bd, J = 8.9, 1H), 7.73 (bs, 1H), 7.64 (bd, J = 9.0, 1H), 7.47 (dd, J = 9.0, 2.2, 1H), 7.25 (d, J = 8.9, 1H), 5.77 (s, 1H).

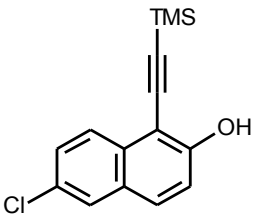
^{13}C NMR (101 MHz, $CDCl_3$): 154.00, 133.21, 131.98, 130.07, 129.95, 129.66, 128.81, 126.78, 117.47, 85.82.

IR ($CHCl_3$): 3579 w, 3480 s, 3063 w, 1620 s, 1496 s, 1349 s, 1262 m, 1183 vs, 1008 w, 981 m, 955 w, 930 vs, 847 m, 809 vs, 650m, 586 w, 556 w, 539 vs cm^{-1}.

APCI MS: 304 ($[M]^+$).

HR APCI MS: calcd for $C_{10}H_6O^{35}ClI$ 303.9146, found 303.9147.

6-Chloro-1-{[trimethylsilyl]ethynyl}naphthalen-2-ol 197



A Schlenk flask was charged with iodide **196** (316 mg, 1.04 mmol), $PdCl_2(PPh_3)_2$ (16.0 mg, 0.02 mmol, 2 mol%), CuI (10.6 mg, 0.056 mmol, 5 mol%), and purged with argon. Then degassed toluene (20 ml) and *N,N*-diisopropylamine (200 µl, 1.43 mmol, 1.4 equiv.) were added. Then degassed (ethynyltrimethyl)silane (300 µl, 2.10 mmol, 2.0 equiv.) was added dropwise to the reaction mixture and the reaction was stirred at 40 °C for 2.5 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane–ethyl acetate 6:1) to afford **197** (77 mg, 27%) as a red oil.

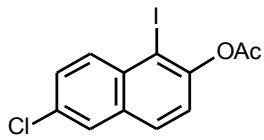
^{1}H NMR (400 MHz, $CDCl_3$): 8.00 (dt, *J* = 8.9, 0.7, 1H), 7.74 (bd, *J* = 2.0, 1H), 7.65 (bd, *J* = 8.7, 1H), 7.46 (dd, *J* = 9.0, 2.2, 1H), 7.21 (d, *J* = 9.0, 1H), 6.17 (s, 1H), 0.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): 156.77, 131.81, 129.75, 128.90, 128.14, 126.92, 126.52, 117.38, 107.91, 103.04, 96.81, 0.10. One quaternary carbon was not found.

ESI MS: 235 ($[M]^+$).

HR ESI MS: calcd for $C_{13}H_{12}O_2{}^{35}Cl$ 235.0520, found 235.0521.

6-Chloro-1-iodonaphthalen-2-yl acetate 198



To a solution of naphthol **196** (834 mg, 2.74 mmol), Et_3N (0.81 ml, 5.77 mmol, 2.1 equiv.) in dichloromethane (20 ml), acetylchloride (220 µl, 3.09 mmol, 1.1 equiv.) was added dropwise under nitrogen at 0 °C. The reaction mixture was stirred at room temperature for 1.5 h. The mixture was quenched with a saturated solution of ammonium chloride (30 ml) and extracted with dichloromethane (2 x 30 ml). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was filtered through a short pad of silica (hexane–diethyl ether 4:1 to 2:1) to afford compound **198** (931 mg, 98%) as off-white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.11 (dt, *J* = 9.1, 0.7, 1H), 7.80 (d, *J* = 2.2, 1H), 7.75 (dt, *J* = 8.7, 0.6, 1H), 7.51 (dd, *J* = 9.1, 2.1, 1H), 7.24 (d, *J* = 8.8, 1H), 2.44 (s, 3H).

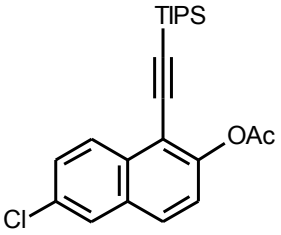
^{13}C NMR (101 MHz, $CDCl_3$): 168.74, 150.27, 133.79, 133.67, 132.54, 132.41, 129.18, 128.95, 126.79, 122.50, 94.34, 21.34.

IR ($CHCl_3$): 3029 w, 3014 w, 1789 w, sh, 1771 s, 1758 w, sh, 1743 w, sh, 1622 w, 1591 w, 1577 w, sh, 1558 w, 1491 m, 1457 w, 1430 w, 1371 m, 1195 vs, 1188 vs, 1154 w, 1086 w, 885 m cm^{-1}.

EI MS: 345 ($M^{+\bullet}$, 32), 303 (100), 286 (1), 177 (16).

HR EI MS: calcd for $C_{12}H_8{}^{35}ClIO_2$, 345.9258, found 345.9255.

6-Chloro-1-{[tris(1-methylethyl)silyl]ethynyl}naphthalen-2-yl acetate 199



A Schlenk flask was charged with iodide **198** (1.0 g, 2.9 mmol), $PdCl_2(PPh_3)_2$ (39 mg, 0.056 mmol, 2 mol%) and CuI (18 mg, 0.095 mmol, 3 mol%) and purged with argon. Then degassed toluene (30 ml) and *N,N*-diisopropylamine (500 µl, 3.57 mmol, 1.2 equiv.) were added and the mixture was heated at 70°C. Then degassed (triisopropylsilyl)acetylene (800 µl, 3.57 mmol, 1.2 equiv.) was added dropwise to the reaction mixture and the reaction was stirred at 70 °C for 3 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane–dichloromethane 4:1) to afford the protected napthol **199** (1.09 g, 94%) as an off-white solid.

1H NMR (400 MHz, CDCl3): 8.28 (dt, *J* = 8.9, 0.7, 1H), 7.82 (bd, *J* = 2.1, 1H), 7.73 (dt, *J* = 8.9, 0.7, 1H), 7.53 (dd, *J* = 8.9, 2.1, 1H), 7.26 (d, *J* = 8.9, 1H), 2.37 (s, 3H), 1.19 (s, 21H).

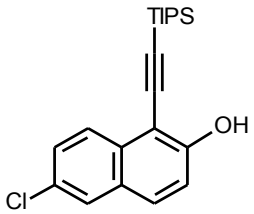
13C NMR (101 MHz, CDCl3): 168.73, 150.85, 132.48, 132.12, 131.79, 128.57, 128.29, 127.88, 126.78, 122.37, 113.78, 102.41, 98.83, 20.95, 18.71, 11.29.

IR ($CHCl_3$): 3062 w, 3031 w, 2959 s, 2945 s, 2892 m, 2866 s, 1766 s, 1620 m, 1586 m, 1500 m, 1463 m, 1383 m, 1368 m, 1363 m, 1091 m, 1071 m, 997 m, 884 s, 829 m, 679 m, 536 w, 464 w, 447 w cm^{-1}.

ESI MS: 423 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{23}H_{29}O_2{}^{35}ClNaSi$ 423.1518, found 423.1518.

6-Chloro-1-{[tris(1-methylethyl)silyl]ethynyl}naphthalen-2-ol 200



Acetate **199** (1.20 g, 2.99 mmol) was dissolved in tetrahydrofuran (20 ml) and methanol (20 ml), and potassium carbonate (846 mg, 6.12 mmol, 2.0 equiv.) was added. The reaction mixture was stirred at room temperature for 3 h, then the reaction mixture was quenched with a saturated solution of ammonium chloride (50 ml) and extracted with dichloromethane (2 x 50 ml). The combined organic layers were dried over anhydrous $MgSO_4$. The solvents were evaporated *in vacuo* to afford napthol **200** (1.07 g, 99%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (dt, J = 8.9, 0.7, 1H), 7.75 (bd, J = 2.1, 1H), 7.66 (dt, J = 9.0, 0.7, 1H), 7.48 (dd, J = 8.9, 2.1, 1H), 7.22 (d, J = 9.0, 1H), 6.22 (s, 1H), 1.19 (m, 21H).

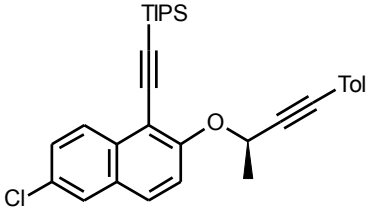
^{13}C NMR (101 MHz, $CDCl_3$): 156.90, 131.88, 129.74, 129.59, 128.92, 128.24, 126.93, 126.47, 117.30, 104.41, 103.39, 98.70, 18.76, 11.22.

IR ($CHCl_3$): 3499 m, 3065 vw, 2959 vs, 2945 vs, 2867 vs, 2134 m, 1615 w, 1592 s, 1581 m, sh, 1508 s, 1493 w, sh, 1463 s, 1384 m, 1370 w, sh, 1360 s, 1269 m, 1158 s, 1144 s, 1089 s, 1075 m, sh, 996 m, 964 m, 900 m, 822 s, 679 s, 658 m, sh, 539 m, 537 m, 465 m, 447 m cm^{-1}.

APCI MS: 359 ($[M+H]^+$).

HR APCI MS: calcd for $C_{21}H_{28}O^{35}ClSi$ 359.1593, found 359.1593.

(–)-[(6-Chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naphthalen-1-yl)ethynyl][tris(1-methylethyl)]silane 201



To a solution of naphthol **200** (860 mg, 2.40 mmol), (–)-(*S*)-**144**[146] (474 mg, 2.96 mmol, 1.2 equiv.), triphenylphosphine (779 mg, 2.97 mmol, 1.2 equiv.) in benzene (10 ml), diisopropyl azodicarboxylate (560 µl, 2.84mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 23 h, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane–ethylacetate 50:1) followed by a flash chromatography

on C-18 reversed-phase silica gel (methanol) to afford the protected diyne (–)-(*R*)-**201** (840 mg, 70%) as a colourless oil, white amorphous solid upon freezing.

Optical rotation: $[\alpha]^{20}_D$ = -20.2° (c 0.291, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 8.26 (dt, *J* = 9.0, 0.7, 1H), 7.75 (bd, *J* = 2.1, 1H), 7.70 (dt, *J* = 9.1, 0.7, 1H), 7.53 (d, *J* = 9.1, 1H), 7.47 (dd, *J* = 9.0, 2.1, 1H), 7.27 – 7.25 (m, 2H), 7.09 – 7.06 (m, 2H), 5.31 (q, *J* = 6.5, 1H), 2.32 (s, 3H), 1.80 (d, *J* = 6.5, 3H), 1.21 (s, 21H).

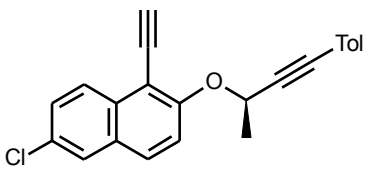
^{13}C NMR (101 MHz, $CDCl_3$): 158.12, 138.67, 133.00, 131.52, 130.14, 129.51, 128.96, 128.48, 127.93, 127.26, 126.56, 119.13, 118.04, 109.14, 101.43, 100.32, 87.41, 86.38, 66.50, 22.52, 21.48, 18.80, 11.38.

IR ($CHCl_3$): 3059 w, sh, 2959 s, sh, 2944 s, 2866 s, 2248 w, sh, 2226 w, 2147 m, 1613 w, sh, 1586 s, 1510 s, 1497 s, 1463 m, 1418 w, sh, 1383 w, sh, 1373 m, 1360 m, 1343 m, sh, 1327 m, 1266 s, 1248 s, 1152 w, 1119 m, 1085 s, 1071 m, sh, 1039 m, 1020 m, 995 m, sh, 902 m, 882 m, 819 s, 664 s, 538 w, 463 w, 447 w cm^{-1}.

ESI MS: 501 ($[M+H]^+$).

HR ESI MS: calcd for $C_{32}H_{38}O^{35}ClSi$ 501.2375, found 501.2376.

(+)-6-Chloro-1-ethynyl-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1yl]oxy}-naphthalene 202



To a solution of the protected diyne (–)-(*R*)-**201** (412 mg, 0.822 mmol) in a mixture of tetrahydrofuran (14 ml) and methanol (0.2 ml), a solution of *n*-tetrabutylammonium fluoride trihydrate (311 mg, 0.986 mmol, 1.2 equiv.) in tetrahydrofuran (6 ml) was added. The reaction mixture was stirred at room temperature for 45 min. Then methanol (10 ml) was added and the mixture was diluted with a saturated solution of ammonium chloride (10 ml), extracted with dichloromethane (3 x 15 ml) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was filtered through a short pad of silica (dichloromethane) to give diyne (+)-(*R*)-**202** (282 mg, 99%) as an amorphous white solid.

Optical rotation: $[\alpha]^{20}_D$ = +37.9° (c 0.274, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 8.23 (dt, *J* = 9.0, 0.7, 1H), 7.77 (bd, *J* = 2.2, 1H), 7.74 (bd, *J* = 9.1, 1H), 7.53 (d, *J* = 9.1, 1H), 7.47 (dd, *J* = 9.0, 2.2, 1H), 7.27 – 7.25 (m, 2H), 7.09 – 7.07 (m, 2H), 5.29 (q, *J* = 6.6, 1H), 3.72 (s, 1H), 2.32 (s, 3H), 1.85 (d, *J* = 6.6, 3H).

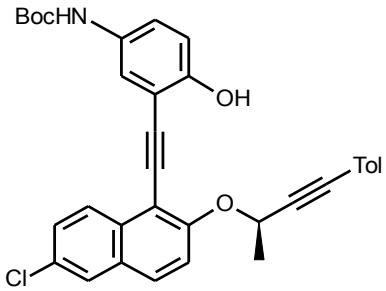
^{13}C NMR (101 MHz, $CDCl_3$): 158.37, 138.75, 133.06, 131.55, 130.38, 129.55, 129.09, 129.00, 128.07, 127.15, 126.64, 119.12, 117.93, 107.68, 87.22, 87.01, 86.60, 77.60, 66.87, 22.48, 21.46.

IR ($CHCl_3$): 3305 m, 2994 w, 2894 w, 2248 w, 2226 w, 2101 w, 1670 w, sh, 1617 w, sh, 1594 w, sh, 1586 vs, 1580 w, sh, 1510 s, 1498 vs, 1466 w, 1359 m, 1343 m, sh, 1269 s, 1247 m, 1163 w, 1119 m, 1085 s, 1037 m, 1020 m, 972 m, 911 m, 819 s, 708 w, 656 m, 536 w cm^{-1}.

ESI MS: 367 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{23}H_{17}O^{35}ClNa$ 367.0860, found 367.0861.

(–)-*tert*-Butyl {3-[(6-chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naphthalen-1-yl)ethynyl]-4-hydroxyphenyl}carbamate 203



A Schlenk flask was charged with iodide **147** (333 mg, 0.994 mmol), $PdCl_2(PPh_3)_2$ (15 mg, 0.021 mmol, 2 mol%) and CuI (9 mg, 0.047 mmol, 5 mol%) and purged with argon. Then degassed toluene (10 ml) and *N,N*-diisopropylamine (170 µl, 1.22 mmol, 1.2 equiv.) were added and the mixture was heated at 50 °C. Then alkyne (+)-(*R*)-**202** (402 mg, 1.17 mmol, 1.2 equiv.) in degassed toluene (10 ml) was slowly added *via* cannula to the reaction mixture and the reaction was stirred at 50 °C for 3 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane–ethyl acetate 20:1) followed by a flash chromatography on C-18 reversed-phase silica gel (methanol) to afford phenol carmabate (–)-(*R*)-**203** (446 mg, 81%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -280° (c 0.348, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (dt, *J* = 9.0, 0.7, 1H), 7.78 (bd, *J* = 2.1, 1H), 7.75 (bdt, *J* = 9.1, 0.7, 1H), 7.69 (bs, 1H), 7.58 (d, *J* = 9.2, 1H), 7.51 (dd, *J* = 8.9, 2.1, 1H), 7.28 – 7.25

(m, 2H), 7.12 (dd, *J* = 8.8, 2.7, 1H), 7.08 – 7.06 (m, 2H), 6.96 (bd, *J* = 8.8, 1H), 6.60 (bs, 1H), 6.37 (bs, 1H), 5.34 (q, *J* = 6.6, 1H), 2.31 (s, 3H), 1.91 (d, *J* = 6.6, 3H), 1.54 (s, 9H).

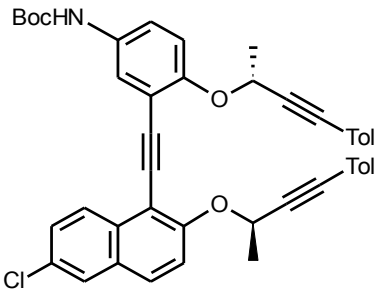
^{13}C NMR (101 MHz, $CDCl_3$): 156.97, 153.47, 153.06, 138.88, 131.61, 131.59, 130.81, 130.41, 129.23, 128.99, 128.89, 128.20, 127.16, 126.66, 121.74, 120.47, 118.85, 115.78, 114.74, 110.13, 107.20, 93.79, 91.55, 87.03, 86.66, 80.50, 66.14, 28.38, 22.46, 21.46.

IR ($CHCl_3$): 3460 w, sh, 3441 m, 2983 w, 2897 w, 2250 w, 2226 w, 2200 w, sh, 1723 m, 1623 w, 1584 m, 1522 m, 1510 m, 1501 s, 1466 w, 1394 m, 1369 m, 1345 m, 1329 w, 1267 m, 1257 m, 1251 m, 1160 vs, 1119 m, 1083 m, 1020 w, 992 w, 820 m, 533 w, 501 w, sh cm^{-1}.

ESI MS: 574 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{34}H_{30}O_4N^{35}ClNa$ 574.1756, found 574.1758.

(–)-*tert*-Butyl(3-[(6-chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-naphthalen-1-yl)ethynyl]-4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-phenyl)carbamate 204



To a solution of phenol (–)-(*R*)-**203** (183 mg, 0.332 mmol), (–)-(*S*)-**144**[146] (74 mg, 0.47 mmol, 1.4 equiv.), triphenylphosphine (114 mg, 0.435 mmol, 1.3 equiv.) in benzene (6 ml), diisopropyl azodicarboxylate (80 µl, 0.41 mmol, 1.2 equiv.) was added dropwise under argon. The reaction was stirred at room temperature for 4 h, then methanol (4 ml) was added and the solvents were evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane–ethyl acetate 50:1) to afford triyne (–)-(*R,R*)-**204** (153 mg, 66%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -145° (c 0.337, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 8.54 (bd, *J* = 9.0, 1H), 7.77 (d, *J* = 2.1, 1H), 7.70 (d, *J* = 8.8, 1H), 7.52 (d, *J* = 9.0, 1H), 7.49 – 7.40 (m, 3H), 7.29 – 7.25 (m, 4H), 7.20 (d, *J* = 8.9, 1H), 7.10 – 7.04 (m, 4H), 6.35 (s, 1H), 5.38 (q, *J* = 6.5, 1H), 5.22 (q, *J* = 6.5, 1H), 2.32 (s, 3H), 2.32 (s, 3H), 1.88 (d, *J* = 6.5, 3H), 1.86 (d, *J* = 6.5, 3H), 1.53 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): 157.18, 154.24, 152.89, 138.61, 138.58, 132.90, 132.20, 131.62, 131.55, 130.41, 129.91, 128.98, 128.95, 128.43, 127.94, 127.71, 126.48, 123.36, 120.42, 119.27, 119.25, 119.12, 115.93, 114.77, 109.99, 95.77, 87.93, 87.67, 87.47, 86.40, 86.26, 80.49, 67.42, 66.14, 28.35, 22.61, 22.59, 21.45 (2C).

IR ($CHCl_3$): 3440 m, 3330 w, 2986 w, 2900 w, 2889 w, 2234 w, 2202 w, sh, 1724 m, 1584 m, 1520 m, sh, 1510 s, 1497 s, 1465 w, 1393 m, 1369 m, 1328 m, 1268 m, 1247 w, sh, 1158 s, 1128 w, 1118 m, 1084 m, 1020 m, 994 w, 977 w, 947 w, 819 m, 710 w, 538 w cm^{-1}.

ESI MS: 716 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{45}H_{40}O_4N^{35}ClNa$ 716.2538, found 716.2542.

Synthesis of oxahelicene amines (–)-(*M*,*R*,*R*)-134, (–)-(*M*,*R*,*R*)-135, **(–)-(*M*,*R*)-166**, **(–)-(*M*,*R*)-167, (–)-(*M*,*R*,*R*)-179a-f, (–)-(*M*,*R*,*R*)-194 and (–)-(*M*,*R*,*R*)-207**

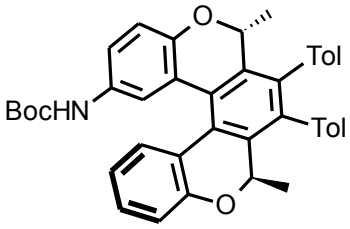
General procedure A *([2+2+2] cycloisomerisation using cobalt catalyst)*: A microwave vial was charged with triynes (–)-(*R*,*R*)-**149**, (–)-(*R*,*R*)-**151**, (+)-(*R*)-**164,** (–)-(*R*)-**165,** (–)-(*R,R*)-**178,** (–)-(*R,R*)-**192** or (–)-(*R*,*R*)-**204** (1.0 equiv.) and CpCo(CO)(fum) (30 - 50 mol%) under argon. Tetrahydrofuran (5 ml) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (3 - 10 mg per 1 ml of THF) were added and the reaction mixture was heated at 140 °C in a microwave reactor for 15 min. Then the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel to furnish the desired cyclic products (–)-(*M*,*R*,*R*)-**150**, (–)-(*M*,*R*,*R*)-**156**, (–)-(*M*,*R*)-**170**, (–)-(*M*,*R*)-**172**, (–)-(*M*,*R*,*R*)-**173**, (–)-(*M*,*R*,*R*)-**181** or (–)-(*M*,*R*,*R*)-**182**.

General procedure B *(Suzuki-Miyaura coupling of chlorohelicenes)*: To a solution of the oxa[5]helicene amine derivative (–)-(*M*,*R*,*R*)-**173,** (–)-(*M*,*R*,*R*)-**181**, or(–)-(*M*,*R*,*R*)-**182,** (1.0 equiv.), pinacol boronate (2.5 equiv.) or boronic acids (2.1 – 3.3 equiv.) and XPhos Pd G2 (5 – 8 mol%) in tetrahydrofuran (2 – 2.8 ml), 0.5 M K_3PO_4 aqueous solution (1.1 – 2.5 equiv.) was added at room temperature. Then argon was bubbled through this biphasic mixture for 15 min. After this period, the reaction vessel was sealed and the mixture was heated at 100 °C and stirred for 1 - 6 h. The reaction mixture was poured into water (20 ml) and extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried over anhydrous $MgSO_4$, the solvents were removed *in vacuo* and the residue was purified by flash

chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) to afford the desired products (–)-(*M*,*R*,*R*)-**179a-f,** (–)-(*M*,*R*,*R*)-**193**, and (–)-(*M*,*R*,*R*)-**205**.

General procedure C *(deprotection of BOC group)*: Trifluoroacetic acid (15 - 33 equiv.) was added to the solution of BOC-protected oxahelicene amines (–)-(*M*,*R*,*R*)-**150**, (–)-(*M*,*R*,*R*)-**156**, (–)-(*M*,*R*)-**170**, (–)-(*M*,*R*)-**172**, (–)-(*M*,*R*,*R*)-**174a-f**, (–)-(*M*,*R*,*R*)-**193** or (–)-(*M*,*R*,*R*)-**205**. (1.0 equiv.) in dichloromethane (3 – 10 ml) at room temperature and the reaction mixture was stirred for 3 – 16 h. After that, it was poured into a saturated solution of $NaHCO_3$ (20 ml) and the product was extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried over anhydrous $MgSO_4$ or Na_2SO_4 and the solvent was removed *in vacuo* to provide the desired oxahelicene amines (–)-(*M*,*R*,*R*)-**134**, (–)-(*M*,*R*,*R*)-**135**, (–)-(*M*,*R*)-**166**, (–)-(*M*,*R*)-**167**, (–)-(*M*,*R*,*R*)-**179a-f**, (–)-(*M*,*R*,*R*)-**194** or (–)-(*M*,*R*,*R*)-**206**.

(–)-(*M*)-*tert*-Butyl[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[1,2-*c*:4,3-*c′*]dichromen-9-yl]carbamate 150



The oxa[5]helicene amine derivative (–)-(*M,R,R*)-**150** was prepared according to the *General procedure A* from triyne (–)-(*R,R*)-**149** (107 mg, 0.176 mmol), CpCo(CO)(fum) (15 mg, 0.052 mmol, 30 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (55 mg) in tetrahydrofuran (5 ml). The purification by flash chromatography on silica gel (hexane-ethyl acetate 100:1) gave the oxa[5]helicene amine derivative (–)-(*M,R,R*)-**150** as a yellow solid (88 mg, 82%).

M.p.: 159-162 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -546° (c 0.286, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.59 (bs, 1H), 7.47 (dd, *J* = 7.9, 1.6, 1H), 7.18 (ddd, *J* = 8.1, 7.3, 1.6, 1H), 7.14 – 7.10 (m, 2H), 7.09 – 7.06 (m, 2H), 7.01 (dd, *J* = 8.1, 1.3, 2H), 6.97 (d, *J* = 8.7, 1H), 6.86 (m, 2H), 6.80 (ddd, *J* = 7.9, 7.3, 1.3, 1H), 6.65 (m, 2H), 6.08 (s, 1H), 5.24 (q, *J* = 6.7, 1H), 5.22 (q, *J* = 6.7, 1H), 2.26 (s, 6H), 1.47 (s, 9H), 0.93 (d, *J* = 6.7, 6H).

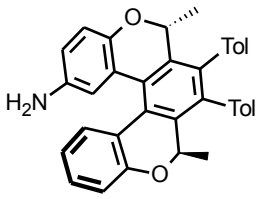
^{13}C NMR (101 MHz, $CDCl_3$): 153.50, 153.03, 149.25, 139.21, 139.02, 137.32, 137.19, 136.06 (2C), 134.77 (2C), 131.54, 130.65 (2C), 129.22, 129.13, 129.01 (2C), 128.57 (2C), 128.37 (2C), 125.21, 124.87, 123.56, 123.21, 120.84, 120.58, 119.67, 119.49, 119.21, 80.31, 72.92, 72.89, 28.31, 21.16 (2C), 18.32, 18.29.

IR ($CHCl_3$): 3438 w, 3081 vw, 3050 w, sh, 2983 m, 1722 s, 1616 w, 1604 w, 1594 vw, 1583 w, 1550 w, sh, 1517 vs, 1495 s, 1485 m, 1420 m, 1393 m, 1381 m, 1368 s, 1309 w, sh, 1298 w, 1272 w, 1185 w, sh, 1159 vs, 1123 w, 1112 w, 1106 w, 1063 s, 1022 w, 1011 w, 945 w, 918 w, 836 m, 518 w, 461 w cm^{-1}.

ESI MS: 632 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{41}H_{39}O_4NNa$ 632.2771, found 632.2772.

(–)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c′*]dichromen-9-amine 134



Oxa[5]helicene amine (–)-(*M,R,R*)-**134** was prepared according to the *General procedure C* from the oxa[5]helicene amine derivative (–)-(*M,R,R*)-**150** (178 mg, 0.292 mmol), trifluoroacetic acid (340 µl, 4.40 mmol, 15 equiv.) in dichloromethane (5 ml) for 16 h. The purification by flash chromatography on C-18 reversed-phase silica gel (methanol) gave oxa[5]helicene amine (–)-(*M,R,R*)-**134** (117 mg, 78%) as a yellowish solid.

M.p.: 161-165 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -629° (c 0.133, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 237 (4.32), 261 (4.28), 316 (3.79), 373 (3.49) nm.

^{1}H NMR (600 MHz, CD_2Cl_2): 7.51 (dd, *J* = 7.9, 1.6, 1H), 7.18 (ddd, *J* = 8.0, 7.7, 1.6, 1H), 7.15 – 7.10 (m, 4H), 6.99 (dd, *J* = 8.0, 1.2, 1H), 6.91 (m, 2H), 6.82 (ddd, *J* = 7.9, 7.7, 1.2, 1H), 6.80 (d, *J* = 8.4, 1H), 6.72 (m, 2H), 6.71 (d, *J* = 2.8, 1H), 6.54 (dd, *J* = 8.4, 2.8, 1H), 5.17 (q, *J* = 6.7, 1H), 5.09 (q, *J* = 6.7, 1H), 3.31 (s, 2H), 2.27 (s, 6H), 0.92 (d, *J* = 6.7, 3H), 0.90 (d, *J* = 6.7, 3H).

^{13}C NMR (151 MHz, CD_2Cl_2): 153.93, 146.17, 140.74, 139.97, 139.41, 137.56, 137.44, 136.64, 136.62, 135.55, 135.51, 131.25, 131.22, 129.76, 129.66, 129.61, 129.46, 128.84,

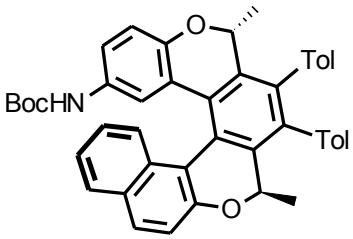
128.83, 128.82, 128.81, 125.94, 125.52, 124.34, 123.88, 121.06, 119.93, 119.48, 116.66, 115.89, 73.28, 72.98, 21.27 (2C), 18.53, 18.37.

IR (KBr): 3444 m, 3368 m, 3080 vw, sh, 3020 m, 2978 m, sh, 2957 s, 1619 m, 1605 m, 1583 m, 1570 vw, 1546 vw, 1517 s, 1493 s, 1485 s, 1450 s, 1404 w, 1379 vw, 1301 m, 1277 m, 1213 vs, 1183 m, 1150 m, 1124 m, 1111 m, 1033 m, 1022 m, 967 w, 956 w, 944 w, 916 w, 821 m, 791 w, 759 m cm^{-1}.

ESI MS: 510 ($[M+H]^+$).

HR ESI MS: calcd for $C_{36}H_{32}O_2N$ 510.2428, found 510.2427.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[*f*]benzo-[1,2-*c*:4,3-*c′*]dichromen-14-yl]carbamate 156



The oxa[6]helicene amine derivative (–)-(*M,R,R*)-**156** was prepared according to the *General procedure A* from triyne (–)-(*R,R*)-**151** (116 mg, 0.176 mmol), CpCo(CO)(fum) (21 mg, 0.071 mmol, 40 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (50 mg) in tetrahydrofuran (5 ml). The purification by flash chromatography on silica gel (hexane-ethyl acetate 95:5) and then on C-18 reversed-phase silica gel (methanol) gave the cyclic product (–)-(*M,R,R*)-**156** (73 mg, 63%) as a yellow solid.

M.p.: 168-171 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -611° (c 0.340, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): 7.75 (d, *J* = 8.7, 1H), 7.67 (bd, *J* = 8.0, 1H), 7.48 (bd, *J* = 8.6, 1H), 7.28 (d, *J* = 8.7, 1H), 7.18 – 7.14 (m, 4H), 7.095 (m, 2H), 6.95 (ddd, *J* = 8.6, 6.8, 1.3, 1H), 6.90 (m, 2H), 6.87 (d, *J* = 8.6, 1H), 6.77 (m, 1H), 6.75 (m, 1H), 6.14 (d, *J* = 2.6, 1H), 5.34 (bs, 1H), 5.32 (q, *J* = 6.7, 1H), 5.27 (q, *J* = 6.7, 1H), 2.28 (s, 6H), 1.39 (s, 9H), 1.00 (d, *J* = 6.7, 3H), 0.99 (d, *J* = 6.7, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 152.81, 152.69, 148.54, 139.58, 138.58, 137.12, 136.70, 136.10, 136.05, 134.94, 134.92, 131.45, 130.86, 130.50, 130.12, 129.86, 129.39, 129.17, 128.99, 128.60, 128.48, 128.44, 128.34, 127.47, 125.68, 125.54, 125.25, 124.20, 123.81,

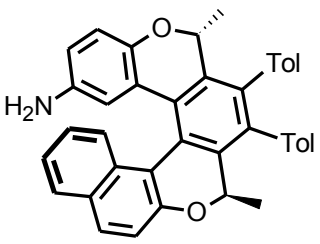
123.58, 120.10, 119.70, 119.10, 118.50, 117.85, 79.89, 73.37, 72.97, 28.24, 21.19 (2C), 18.64, 17.74.

IR (KBr): 3492 s, sh, 3437 vs, br, 3280 m, sh, 2978 w, 2927 w, 1732 m, 1716 m, 1620 m, 1593 w, 1542 w, sh, 1523 w, sh, 1517 m, 1391 m, sh, 1382 m, 1253 m, 1243 m, 1161 s, 1153 m, sh, 1076 w, 1049 w, 920 w, sh, 843 w, 813 w, 770 w, br, sh, 589 w, 534 w, 470 w cm^{-1}.

ESI MS: 682 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{45}H_{41}O_4NNa$ 682.2928, found 682.2930.

(–)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[*f*]benzo-[1,2-*c*:4,3-*c′*]-dichromen-14-amine 135



Oxa[6]helicene amine (–)-(*M,R,R*)-**135** was prepared according to the *General procedure C* from the oxa[6]helicene amine derivative (–)-(*M,R,R*)-**156** (157 mg, 0.238 mmol) and trifluoroacetic acid (280 µl, 3.66 mmol, 15.0 equiv.) in dichloromethane (6 ml) for 16 h. The purification by flash chromatography on silica gel (hexane-ethyl acetate 7:1) gave oxa[6]helicene amine (–)-(*M,R,R*)-**135** (103 mg, 77%) as a pale orange solid.

M.p.: 152-157 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -687° (c 0.186, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 244 (4.76), 291 (4.18), 320 (3.99), 358 (4.13) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 530 nm.

^{1}H NMR (400 MHz, CD_2Cl_2): 7.78 (d, *J* = 8.7, 1H), 7.72 – 7.70 (m, 1H), 7.54 – 7.51 (m, 1H), 7.28 (d, *J* = 8.7, 1H), 7.21 – 7.17 (m, 2H), 7.16 – 7.12 (m, 3H), 7.00 (ddd, *J* = 8.4, 6.8, 1.4, 1H), 6.97 – 6.94 (m, 2H), 6.85 – 6.81 (m, 2H), 6.71 (d, *J* = 8.4, 1H), 6.25 (dd, *J* = 8.4, 2.7, 1H), 5.77 (d, *J* = 2.7, 1H), 5.26 (q, *J* = 6.7, 1H), 5.16 (q, *J* = 6.7, 1H), 2.69 (bs, 2H), 2.29 (s, 6H), 0.98 (d, *J* = 6.7, 3H), 0.96 (d, *J* = 6.7, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): 153.14, 145.52, 140.75, 140.14, 139.36, 137.27, 137.08, 136.69, 136.61, 135.66, 135.60, 131.42, 131.07, 130.44, 130.34, 130.04, 129.73, 129.57,

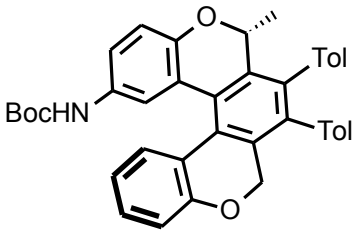
128.87 (2C), 128.80, 128.73, 128.01, 126.82, 125.94, 125.56, 125.11, 124.09, 123.81, 120.09, 119.09, 118.68, 115.74, 115.12, 73.83, 72.95, 21.29 (2C), 18.72, 17.92.

IR (KBr): 3436 s, 3362 m, sh, 3049 w, 2980 w, 1619 s, 1591 m, 1516 s, 1491 s, 1430 m, sh, 1404 vw, 1382 m, 1365 m, 1183 w, 1110 w, 1022 w, 1014 m, 842 m, 810 s, 711 w cm^{-1}.

ESI MS: 560 ($[M+H]^+$).

HR ESI MS: calcd for $C_{40}H_{34}O_2N$ 560.2584, found 560.2585.

(–)-(*M*)-*tert*-Butyl[(5*R*)-5-methyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[1,2-*c*:4,3*c*']dichromen-9-yl]carbamate 170



Oxa[5]helicene (–)-(*M,R*)-**170** was prepared according to the *General procedure A* from triyne (–)-(*R*)-**164** (126 mg, 0.212 mmol), CpCo(CO)(fum) (20 mg, 0.068 mmol, 32 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (49 mg) in tetrahydrofuran (5 ml). The residue was flash chromatographed on silica gel (hexane–ethyl acetate 30:1) gave oxa[5]helicene (–)-(*M,R*)-**170** as a yellow solid (75 mg, 60%).

M.p.:137.8-141.8 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -434° (0.340, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 7.61 (bs, 1H), 7.45 (dd, *J* = 7.9, 1.6, 1H), 7.19 (ddd, *J* = 8.0, 7.3, 1.6, 1H), 7.05 (dd, *J* = 8.0, 1.6, 1H), 7.04 (bs, 1H), 7.02 – 6.96 (m, 4H), 6.98 (d, *J* = 8.7, 1H), 6.95 – 6.89 (m, 3H), 6.83 (ddd, *J* = 7.9, 7.3, 1.6, 1H), 6.71 (m, 1H), 6.10 (bs, 1H), 5.09 (q, *J* = 6.6, 1H), 4.81 (d, *J* = 14.2, 1H), 4.49 (d, *J* = 14.2, 1H), 2.26 (s, 3H), 2.25 (s, 3H), 1.47 (s, 9H), 1.07 (d, *J* = 6.6, 3H).

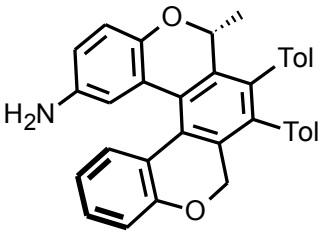
^{13}C NMR (151 MHz, $CDCl_3$): 156.47, 153.02, 149.34, 139.40, 137.71, 136.98, 136.32, 136.27, 135.87, 134.79, 134.77, 131.58, 130.74, 129.74, 129.23, 129.12, 129.06 (2C), 128.64, 128.56, 128.53, 128.20, 126.48, 124.74, 124.07, 123.48, 121.19, 120.69, 119.50 (2C), 117.77, 80.18, 72.92, 68.23, 28.30, 21.17, 21.15, 18.92.

IR ($CHCl_3$): 3438 w, 2982 m, 2928 m, 1722 s, 1616 w, 1603 w, 1583 w, 1524 s, sh, 1517 vs, 1512 s, sh, 1496 s, 1461 m, 1448 w, 1393 w, 1381 w, 1369 m, 1255 m, 1182 w, sh, 1159 vs, 1121 w, 1056 w, 1037 m, 1022 w, 823 w, 804 w, 542 w, 442 w cm^{-1}.

ESI MS: 618 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{40}H_{37}O_4NNa$ 618.2615, found 618.2615.

(–)-(*M*)-(5*R*)-5-Methyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c*']-dichromen-9-amine 166



Amino[5]oxahelicene (–)-(*M,R*)-**166** was prepared according to the *General procedure C* from helicene (–)-(*M,R*)-**170** (130 mg, 0.218 mmol), trifluoroacetic acid (250 µl, 3.27 mmol, 15.0 equiv.) in dichloromethane (4 ml) for 16 h. The residue was flash chromatographed on silica gel (hexane–ethyl acetate 4:1) gave amino[5]oxahelicene (–)-(*M,R*)-**166** (81 mg, 76%) as a pale brown solid.

M.p.: 283.5 – 287.1°C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -488° (c 0.372, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 212 (5.08), 268 (4.86), 305 (4.40), 374 (4.10) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 360 nm): λ_{max} = 500 nm.

^{1}H NMR (600 MHz, CD_2Cl_2): 7.50 (dd, *J* = 7.8, 1.6, 1H), 7.19 (ddd, *J* = 8.1, 7.3, 1.6, 1H), 7.07 – 6.99 (m, 5H), 7.04 (dd, *J* = 8.1, 1.3, 1H), 6.97 (m, 1H), 6.93 (m, 1H), 6.85 (ddd, *J* = 7.8, 7.3, 1.3, 1H), 6.80 (d, *J* = 8.5, 1H), 6.78 (m, 1H), 6.73 (d, *J* = 2.7, 1H), 6.55 (dd, *J* = 8.5, 2.7, 1H), 4.97 (q, *J* = 6.6, 1H), 4.73 (d, *J* = 14.0, 1H), 4.48 (d, *J* = 14.0, 1H), 3.31 (bs, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 1.04 (d, *J* = 6.6, 3H).

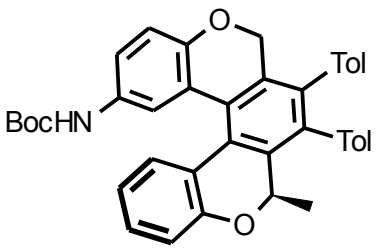
^{13}C NMR (151 MHz, CD_2Cl_2): 156.84, 146.21, 140.76, 140.12, 137.74, 137.26, 136.83, 136.81, 136.21, 135.54, 135.51, 131.37, 130.27, 129.73, 129.68, 129.55, 129.37, 128.98, 128.91, 128.89, 128.54, 126.72, 125.75, 124.65, 124.21, 121.39, 119.91, 117.95, 116.76, 115.73, 72.95, 68.66, 21.27, 21.26, 18.96.

IR ($CHCl_3$): 3435 m, 3362 m, 2972 m, 2923 m, 2854 m, 1623 m, 1585 m, 1550 m, 1517 m, 1494 s, 1485 s, 1455 m, 1427 m, 1364 m, 1212 s, 1033 m, 1022 m, 818 m, 757 s, 529 m cm^{-1}.

ESI MS: 496 ($[M+H]^+$).

HR ESI MS: calcd for $C_{35}H_{30}O_2N$ 496.2271, found 496.2271.

(–)-(*M*)-*tert*-Butyl[(2*R*)-2-methyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c*']dichromen-9-yl]carbamate 172



Oxa[5]helicene (–)-(*M,R*)-**172** was prepared according to the *General procedure A* from triyne (–)-(*R*)-**165** (129 mg, 0.217 mmol), CpCo(CO)(fum) (21 mg, 0.071 mmol, 33 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (30 mg) in tetrahydrofuran (5 ml). The solvent was evaporated *in vacuo* and the crude mixture was flash chromatographed on silica gel (hexane–ethyl acetate 25:1) gave oxa[5]helicene (–)-(*M,R*)-**172** (87 mg, 67%) as a yellow solid.

M.p.: 151.6-154.4 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -439° (0.366, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.55 (bs, 1H), 7.48 (dd, *J* = 7.9, 1.6, 1H), 7.19 (ddd, *J* = 8.0, 7.3, 1.6, 1H), 7.06 – 6.89 (m, 10H), 6.81 (ddd, *J* = 7.8, 7.3, 1.3, 1H), 6.72 (dt, *J* = 7.8, 1.2, 1H), 6.08 (s, 1H), 5.12 (q, *J* = 6.6, 1H), 4.78 (d, *J* = 14.2, 1H), 4.44 (d, *J* = 14.2, 1H), 2.27 (s, 3H), 2.25 (s, 3H), 1.47 (s, 9H), 1.07 (d, *J* = 6.6, 3H).

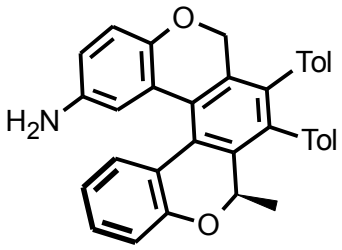
^{13}C NMR (101 MHz, $CDCl_3$): 153.59, 153.04, 152.36, 139.21, 137.58, 137.09, 136.31, 136.26, 136.01, 134.78 (2C), 131.76, 130.73, 129.75, 129.26, 129.11, 129.10, 129.06, 128.63, 128.57, 128.52, 128.20, 126.18, 125.07, 124.43, 123.14, 120.87, 120.65, 119.84, 119.21, 118.03, 80.37, 72.88, 68.41, 28.29, 21.18, 21.15, 18.94.

IR ($CHCl_3$): 3437 w, 1723 vs, 1524 s, sh, 1518 vs, 1513 m, sh, 1495 s, 1458 vw, 1446 w, 1393 m, 1381 m, 1369 m, 1257 m, 1182 m, sh, 1159 vs, 1120 w, 1062 m, 1023 m, 823 w, 442 w cm^{-1}.

ESI MS: 618 ([M+Na]$^+$).

HR ESI MS: calcd for $C_{40}H_{37}O_4NNa$: 618.2615, found 618.2615.

(–)-(*M*)-(2*R*)-2-Methyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c*']di-chromen-9-amine 167



Aminooxa[5]helicene (–)-(*M,R*)-**167** was prepared according to the *General procedure C* from helicene (–)-(*M,R*)-**172** (97 mg, 0.16 mmol), trifluoroacetic acid (200 µl, 2.61 mmol, 16.0 equiv.) in dichloromethane (3 ml) for 7 h. The residue was flash chromatographed on silica gel (hexane–ethyl acetate 10:1) gave aminooxa[5]helicene (–)-(*M,R*)-**167** (64 mg, 80%) as a yellowish solid.

M.p.: 282-287°C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -470° (c 0.418, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 212 (5.10), 239 (4.91), 268 (4.88), 318 (4.40), 370 (4.07) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 360 nm): λ_{max} = 515 nm.

^{1}H NMR (600 MHz, CD_2Cl_2): 7.53 (dd, *J* = 7.8, 1.6, 1H), 7.20 (ddd, *J* = 8.0, 7.3, 1.6, 1H), 7.05 – 7.02 (m, 5H) , 7.00 (dd, *J* = 8.0, 1.2, 1H), 6.97 (m, 1H), 6.94 (m, 1H), 6.85 (d, *J* = 8.4, 1H), 6.83 (ddd, *J* = 7.8, 7.3, 1.2, 1H), 6.78 (m, 1H), 6.70 (bd, *J* = 2.7, 1H), 6.54 (dd, *J* = 8.4, 2.7, 1H), 5.05 (q, *J* = 6.6, 1H), 4.66 (d, *J* = 14.0, 1H), 4.40 (d, *J* = 14.0, 1H), 3.31 (s, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 1.05 (d, *J* = 6.6, 3H).

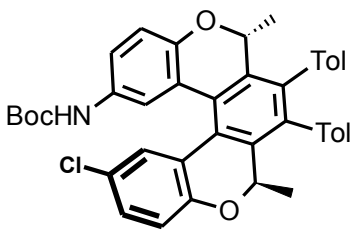
^{13}C NMR (151 MHz, CD_2Cl_2): 153.97, 149.30, 141.01, 139.57, 137.86, 137.14, 136.86, 136.84, 136.76, 135.54, 135.50, 131.40, 130.26, 129.71, 129.63, 129.58, 129.53, 129.00, 128.89, 128.88, 128.56, 127.15, 125.34, 125.15, 123.75, 121.08, 119.45, 118.32, 116.43, 115.71, 73.26, 68.74, 21.28, 21.26, 19.12.

IR ($CHCl_3$): 3449 m, 3367 m, 3216 m, 3021 m, 2980 m, 2924 m, 2864 m, 1622 m, 1604 m, 1583 m, 1493 s, 1486 m, 1452 m, 1427 m, 1366 m, 1213 s, 1060 m, 1024 m, 754 s, 531 m cm^{-1}.

ESI MS: 496 ($[M+H]^+$).

HR ESI MS: calcd for $C_{35}H_{30}O_2N$ 496.2271, found 496.2270.

(–)-(*M*)-*tert*-Butyl[(2*R*,5*R*)-12-chloro-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c′*]dichromen-9-yl]carbamate 173



The oxa[5]helicene amine derivative (–)-(*M,R,R*)-**173** was prepared according to the *General procedure A* from triyne (–)-(*R,R*)-**178** (100 mg, 0.156 mmol), CpCo(CO)(fum) (23 mg, 0.078 mmol, 50 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (50 mg) in tetrahydrofuran (5 ml). The purification by flash chromatography on silica gel (hexane-ethyl acetate 49:1) gave the oxa[5]helicene amine derivative (–)-(*M,R,R*)-**173** (74 mg, 74%) as a yellowish solid.

Alternatively, *$Ni(PPh_3)_2(CO)_2$*: A microwave vial was charged with triyne (–)-(*R,R*)-**178** (50 mg, 0.078 mmol), $Ni(PPh_3)_2(CO)_2$ (18 mg, 0.028 mmol, 36 mol%) and toluene (5 ml) and argon was bubbled through the reaction mixture for 15 min. Then it was heated at 110 °C under stirring for 15 min. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 10:1) to obtain the oxa[5]helicene amine derivative (–)-(*M,R,R*)-**173** (35 mg, 70%) as a pale yellow solid.

M.p.: 171-174 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -671° (c 0.250, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.48 – 7.40 (m, 2H), 7.20 (bd, *J* = 2.6, 1H), 7.14 – 7.05 (m, 5H), 6.98 (d, *J* = 8.7, 1H), 6.94 (d, *J* = 8.5, 1H), 6.89 – 6.84 (m, 2H), 6.66 – 6.63 (m, 2H), 6.18 (bs, 1H), 5.23 (q, *J* = 6.7, 1H), 5.22 (q, *J* = 6.7, 1H), 2.26 (s, 6H), 1.48 (s, 9H), 0.95 (d, *J* = 6.7, 3H), 0.93 (d, *J* = 6.7, 3H).

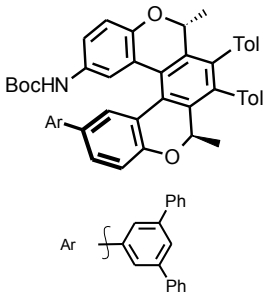
^{13}C NMR (101 MHz, $CDCl_3$): 153.01, 152.03, 149.33, 139.33, 138.85, 137.84, 137.38, 136.18 (2C), 134.58 (2C), 131.70, 130.60, 130.53, 128.95, 128.94, 128.82, 128.79, 128.62, 128.59, 128.43, 128.41, 125.76, 125.14, 124.55, 124.00, 122.85, 121.23, 120.40, 119.59 (2C), 80.30, 73.15, 72.85, 28.30, 21.17 (2C), 18.34, 18.26.

IR ($CHCl_3$): 3439 w, 2983 m, 2871 w, 1723 m, 1616 w, 1594 w, 1517 s, 1481 m, 1454 w, sh, 1431 m, 1408 w, 1393 m, 1368 m, 1328 w, 1260 m, 1257 m, sh, 1159 s, 1102 m, 1089 w, 1061 m, 1022 w, 855 m, 821 m, 696 w, 584 w, 469 m cm^{-1}.

ESI MS: 666 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{41}H_{38}O_4N^{35}ClNa$ 666.2381, found 666.2383.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-(1,1':3',1''-terphenyl-5'-yl)-2,5-dihydrobenzo[1,2-c:4,3-c']dichromen-9-yl]carbamate 174a



The oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174a** was prepared according to the *General procedure B* from the chloro derivative (–)-(*M,R,R*)-**173** (145 mg, 0.225 mmol), 2([1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane acid **213**[167] (205 mg, 0.575 mmol, 2.6 equiv.), XPhos Pd G2 (13 mg, 0.017 mmol, 7 mol%) and K_3PO_4 (0.5 M in water, 0.50 ml, 0.25 mmol, 1.1 equiv.) in tetrahydrofuran (2.8 ml) at 100 °C for 6 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (–)-(*M,R,R*)-**174a** (149 mg, 79%) as a white solid.

M.p.: 185-190 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -596° (c 0.311, $CHCl_3$).

^{1}H NMR (400 MHz, CD_2Cl_2): 7.85 (bd, *J* = 2.3, 1H), 7.73 (t, *J* = 1.7, 1H), 7.65 – 7.62 (m, 4H), 7.55 (dd, *J* = 8.4, 2.3, 1H), 7.52 – 7.47 (m, 7H), 7.43 – 7.37 (m, 3H), 7.18 – 7.10 (m, 5H), 6.99 (d, *J* = 8.8, 1H), 6.94 – 6.91 (m, 2H), 6.74 (dt, *J* = 7.9, 2.0, 2H), 6.26 (bs, 1H), 5.24 (q, *J* = 6.7, 1H), 5.17 (q, *J* = 6.7, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 1.30 (s, 9H), 1.00 (d, *J* = 6.7, 3H), 0.95 (d, *J* = 6.7, 3H).

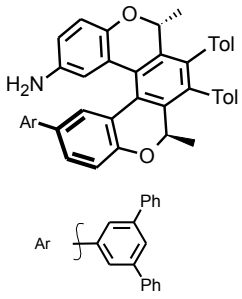
^{13}C NMR (101 MHz, CD_2Cl_2): 153.78, 152.95, 149.61, 142.56, 142.45, 141.29, 139.96, 139.50, 137.81, 136.73, 136.72, 135.35, 135.32, 134.10, 132.55, 131.17, 129.57, 129.56, 129.24 (2C), 128.88, 128.87, 128.85, 128.63, 128.43, 127.94, 127.60 (2C), 125.48, 125.43, 124.79, 124.76, 124.17, 123.70, 120.50, 120.05, 119.95, 118.98, 80.44, 73.52, 73.29, 28.25, 21.28 (2C), 18.70, 18.49, one quaternary carbon was not identified.

IR ($CHCl_3$): 3434 w, 3060 w, 2983 m, 1722 m, 1615 w, 1595 m, 1547 w, sh, 1517 s, 1498 m, 1490 m, 1455 w, 1441 w, 1413 w, 1404 w, sh, 1393 w, 1369 m, 1329 w, 1267 w, sh, 1254 m, 1186 w, sh, 1159 s, 1108 w, 1089 w, 1076 vw, 1021 w, 955 w, 916 w, 899 w, 822 m, 809 w, 614 w, 534 w cm^{-1}.

ESI MS: 860 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{59}H_{51}O_4NNa$ 860.3710, found 860.3716.

(–)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-12-(1,1':3',1''-terphenyl-5'-yl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-amine 179a



The oxa[5]helicene amine (–)-(*M,R,R*)-**179a** was prepared according to the *General procedure C* from the oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174a** (115 mg, 0.14 mmol) and trifluoroacetic acid (350 µl, 4.6 mmol, 33 equiv.) in dichloromethane (3 ml) for 3 h. The purification by flash chromatography on silica gel (hexane-ethyl acetate 10:1) gave oxa[5]helicene amine (–)-(*M,R,R*)-**179a** (98 mg, 97%) as a yellowish solid.

M.p.: 169-171 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -578° (c 0.346, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 262 (4.93), 345 (3.87) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 380 nm): λ_{max} = 498 nm.

^{1}H NMR (400 MHz, CD_2Cl_2): 7.99 (bd, *J* = 2.2, 1H), 7.76 (t, *J* = 1.7, 1H), 7.70 – 7.67 (m, 4H), 7.63 (d, *J* = 1.7, 2H), 7.55 (dd, *J* = 8.3, 2.2, 1H), 7.52 – 7.47 (m, 4H), 7.43 – 7.38 (m, 2H), 7.17 – 7.10 (m, 5H), 6.94 – 6.91 (m, 3H), 6.89 (bd, *J* = 8.4, 1H), 6.76 – 6.73 (m, 2H), 6.55 (dd, *J* = 8.5, 2.7, 1H), 5.23 (q, *J* = 6.7, 1H), 5.12 (q, *J* = 6.7, 1H), 3.28 (bs, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 1.00 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): 153.73, 146.41, 142.47, 142.41, 141.31, 140.64, 140.13, 139.29, 137.79, 137.51, 136.67, 136.63, 135.48, 135.46, 133.91, 131.23, 131.17, 129.64, 129.58, 129.13 (2C), 128.85, 128.81, 128.80, 128.37, 127.92, 127.67 (2C), 126.02, 125.35,

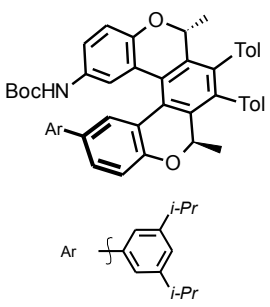
124.83, 124.66, 124.45, 123.85, 120.15, 119.82, 117.31, 115.78, 73.53, 72.98, 21.28 (2C), 18.72, 18.38.

IR ($CHCl_3$): 3453 w, 3383 w, 3060 w, sh, 3024 m, 1797 s, 1619 m, 1595 m, 1518 m, 1497 s, 1426 m, 1441 m, 1413 m, 1405 w, sh, 1306 w, sh, 1267 m, 1249 m, 1183 w, 1109 m, 1086 m, 1076 m, 1030 m, 1021 m, 1009 m, 957 w, 816 m, 614 m, 534 m cm^{-1}.

ESI MS: 738 ($[M+H]^+$).

HR ESI MS: calcd for $C_{54}H_{44}O_2N$ 738.3367, found 738.3367.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-12-[3,5-bis(1-methylethyl)phenyl]-2,5-dimethyl-3,4-bis(4-methyl-phenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c′*]dichromen-9-yl]carbamate 174b



The oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174b** was prepared according to the *General procedure B* from the chloro derivative (–)-(*M,R,R*)-**173** (120 mg, 0.187 mmol), 1,3-diisopropyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl) benzene **214**[168] (131 mg, 0.455 mmol, 2.5 equiv.), XPhos Pd G2 (11 mg, 0.014 mmol, 8 mol%) and K_3PO_4 (0.5 M in water, 0.95 ml, 0.48 mmol, 2.5 equiv.) in tetrahydrofuran (2.5 ml) at 100 °C for 2 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (–)-(*M,R,R*)-**174b** (128 mg, 89%) as a white solid.

M.p.: 161-166 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -657° (c 0.304, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (bs, 1H), 7.72 (bd, *J* = 2.2, 1H), 7.42 (dd, *J* = 8.3, 2.2, 1H), 7.20 – 7.03 (m, 7H), 6.99 – 6.97 (m, 3H), 6.90 – 6.80 (m, 2H), 6.67 – 6.65 (m, 2H), 6.15 (s, 1H), 5.28 (q, *J* = 6.7, 1H), 5.23 (q, *J* = 6.7, 1H), 2.86 (sept, *J* = 6.9, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 1.40 (s, 9H), 1.24 (d, *J* = 7.0, 6H), 1.22 (d, *J* = 7.0, 6H), 0.97 (d, *J* = 6.7, 3H), 0.95 (d, *J* = 6.7, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): 152.85, 152.79, 149.33, 149.31, 140.81, 139.35, 138.95, 137.30, 137.24, 136.07 (2C), 134.78, 134.75, 134.47, 131.86, 130.71, 130.64, 129.04, 129.02, 128.59, 128.58, 128.38, 128.37, 128.24, 127.90, 125.23, 124.90, 123.77, 123.48,

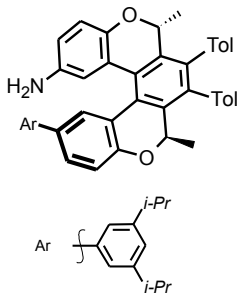
123.06, 122.25, 120.48, 119.67, 119.36, 119.15, 80.27, 73.10, 72.96, 34.29, 28.21, 24.03, 21.18 (2C), 18.52, 18.31.

IR ($CHCl_3$): 3433 w, 3086 vw, 3050 w, sh, 2979 m, 2964 m, 2890 vw, 2870 w, 1722 s, 1615 w, 1597 w, 1549 w, sh, 1517 vs, 1467 m, 1455 m, sh, 1427 m, 1404 w, 1393 w, 1384 w, 1369 m, 1301 w, 1184 m, sh, 1159 vs, 1112 w, 1107 w, 1101 w, 1022 w, 956 vw, 946 vw, 887 w, 824 m, 809 w, 714 w, 694 vw cm^{-1}.

ESI MS: 792 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{53}H_{55}O_4NNa$ 792.4023, found 792.4026.

(–)-(*M*)-(2*R*,5*R*)-12-[3,5-bis(1-Methylethyl)phenyl]-2,5-dimethyl-3,4-bis(4-methyl-phenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c′*]dichromen-9-amine 179b



Oxa[5]helicene amine (–)-(*M,R,R*)-**179b** was prepared according to the *General procedure C* from the oxa[5]helicene derivative (–)-(*M,R,R*)-**174b** (104 mg, 0.135 mmol) and trifluoroacetic acid (260 µl, 3.40 mmol, 25 equiv.) in dichloromethane (10 ml) for 16 h. Evaporation of solvent provided the desired oxa[5]helicene amine (–)-(*M,R,R*)-**179b** (89 mg, 98%) as a yellowish solid, which was used without further purification.

M.p.: 148-153 °C (dichloromethane).

Optical rotation: $[\alpha]^{20}_D$ = -668° (c 0.112, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 258 (4.90), 340 (4.02) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 495 nm.

^{1}H NMR (600 MHz, CD_2Cl_2): 7.82 (d, *J* = 2.3, 1H), 7.44 (dd, *J* = 8.3, 2.3, 1H), 7.16 – 7.10 (m, 4H), 7.08 (d, *J* = 1.7, 2H), 7.05 (d, *J* = 8.3, 1H), 6.99 (t, *J* = 1.7, 1H), 6.92 (m, 2H), 6.86 (bd, *J* = 8.6, 1H), 6.85 (bd, *J* = 2.6, 1H), 6.75 – 6.73 (m, 2H), 6.61 (dd, *J* = 8.6, 2.6, 1H), 5.20 (q, *J* = 6.7, 1H), 5.11 (q, *J* = 6.7, 1H), 3.34 (bs, 2H), 2.87 (sept, *J* = 6.9, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 1.25 (d, *J* = 6.9, 6H), 1.23 (d, *J* = 6.9, 6H), 0.97 (d, *J* = 6.7, 3H), 0.93 (d, *J* = 6.7, 3H).

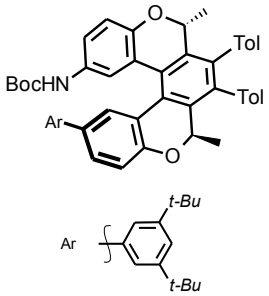
^{13}C NMR (151 MHz, CD_2Cl_2): 153.22, 149.77, 146.30, 141.09, 140.77, 140.05, 139.25, 137.61, 137.41, 136.64, 136.61, 135.51, 135.49, 134.55, 131.24, 131.19, 129.65, 129.60, 128.84, 128.83, 128.80, 128.795, 128.67, 128.05, 126.00, 125.50, 124.48, 123.78, 123.62, 122.60, 120.13, 119.50, 116.94, 115.80, 73.46, 72.98, 34.74, 24.25, 21.273, 21.268, 18.68, 18.36.

IR ($CHCl_3$): 3425 w, 3385 w, 2963 m, 2928 w, 2871 w, 1616 w, 1604 vw, sh, 1583 w, 1544 w, 1496 m, sh, 1490 m, 1458 m, 1428 m, 1366 m, 1330 w, 1299 w, 1149 m, 1112 vw, 1088 w, 1063 m, 895 w, 875 w, 841 w, 815 w, 567 w, 524 vw, 449 vw cm^{-1}.

ESI MS: 670 ($[M+H]^+$).

HR ESI MS: calcd for $C_{48}H_{48}O_2N$ 670.3680, found 670.3681.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-12-(3,5-di-*tert*-butylphenyl)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c′*]dichromen-9-yl]carbamate 174c



The oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174c** was prepared according to the *General procedure B* from the chloro derivative (–)-(*M,R,R*)-**173** (100 mg, 0.156 mmol), 3,5-di-*tert*-butylphenyl boronic acid **215**[169] (119 mg, 0.509 mmol, 3.3 equiv.), XPhos Pd G2 (6.7 mg, 0.0085 mmol, 5 mol%) and K_3PO_4 (0.5 M in water, 0.78 ml, 0.39 mmol, 2.5 equiv.) in tetrahydrofuran (2.5 ml) at 100 °C for 6 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (–)-(*M,R,R*)-**174c** (102 mg, 82%) as a white solid.

M.p.: 142-145 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -647° (c 0.359, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 7.80 (bs, 1H), 7.70 (d, *J* = 2.2, 1H), 7.44 (dd, *J* = 8.3, 2.2, 1H), 7.33 (t, *J* = 1.8, 1H), 7.16 – 7.08 (m, 5H), 7.12 (d, *J* = 1.8, 2H), 7.08 (d, *J* = 8.3, 1H), 7.02 (d, *J* = 8.9, 1H), 6.87 (m, 2H), 6.66 (m, 2H), 6.13 (bs, 1H), 5.29 (q, *J* = 6.7, 1H), 5.23 (q, *J* = 6.7, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.40 (s, 9H), 1.31 (s, 18H), 0.97 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

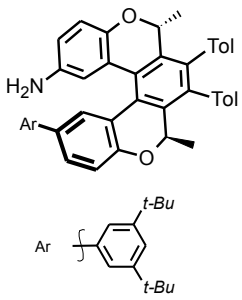
^{13}C NMR (151 MHz, $CDCl_3$): 152.81 (2C), 151.07, 149.25, 140.18, 139.33, 139.07, 137.29, 137.24, 136.08 (2C), 135.07, 134.80 (2C), 131.78, 130.73, 130.68, 129.06 (2C), 128.59 (2C), 128.38 (2C), 128.26, 128.04, 125.30, 124.93, 123.77, 123.22, 121.20, 120.78, 120.58, 119.60, 119.48, 119.07, 80.28, 73.12, 72.96, 34.93, 31.45, 28.22, 21.17 (2C), 18.50, 18.34.

IR ($CHCl_3$): 3435 w, 3028 w, 2967 s, 2906 m, sh, 2868 m, 1723 s, 1607 w, sh, 1594 m, 1570 vw, sh, 1523 s, sh, 1517 vs, 1489 s, 1478 m, sh, 1403 w, 1381 w, sh, 1368 s, 1365 vw, sh, 1255 m, 1249 m, 1183 w, sh, 1159 vs, 1127 m, 1022 vw, 1008 m, 877 m, 856 w, 843 w, 825 m, 715 w, 469 w cm^{-1}.

ESI MS: 820 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{55}H_{59}O_4NNa$ 820.4336, found 820.4342.

(–)-(*M*)-(2*R*,5*R*)-12-(3,5-di-*tert*-Butylphenyl)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c′*]dichromen-9-amine 179c



Oxa[5]helicene amine (–)-(*M,R,R*)-**179c** was prepared according to the *General procedure C* from the oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174c** (98 mg, 0.13 mmol) and trifluoroacetic acid (240 µl, 3.1 mmol, 26 equiv.) in dichloromethane (10 ml) for 16 h. Evaporation of solvent provided oxa[5]helicene amine (–)-(*M,R,R*)-**179c** (73 mg, 85%) as a light orange solid, which was used without further purification.

M.p.: 168-172 °C (dichloromethane).

Optical rotation: $[\alpha]^{20}_D$ = -669° (c 0.345, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 257 (5.01), 343 (4.16) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 493 nm.

^{1}H NMR (400 MHz, CD_2Cl_2): 7.80 (bd, *J* = 2.2, 1H), 7.46 (dd, *J* = 8.3, 2.3, 1H), 7.34 (t, *J* = 1.7, 1H), 7.21 (d, *J* = 1.8, 2H), 7.19 – 7.09 (m, 4H), 7.07 (d, *J* = 8.3, 1H), 6.93 – 6.90 (m, 2H), 6.88 – 6.82 (m, 2H), 6.76 – 6.71 (m, 2H), 6.57 (dd, *J* = 8.5, 2.7, 1H), 5.21 (q, *J* = 6.7, 1H), 5.11 (q, *J* = 6.7, 1H), 3.30 (bs, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 1.32 (s, 18H), 0.97 (d, *J* = 6.7, 3H), 0.93 (d, *J* = 6.7, 3H).

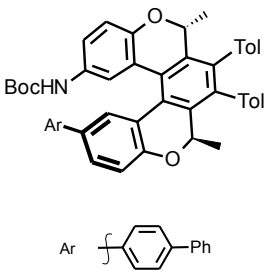
^{13}C NMR (101 MHz, CD_2Cl_2): 153.21, 151.50, 146.19, 140.60, 140.48, 140.00, 139.33, 137.58, 137.37, 136.63, 136.59, 135.53, 135.48, 135.10, 131.24, 131.21, 129.64, 129.61, 128.83 (2C), 128.80, 128.79, 128.65, 128.19, 126.03, 125.56, 124.47, 123.75, 121.47, 121.14, 120.02, 119.59, 117.15, 115.74, 73.47, 72.97, 35.27, 31.63, 21.28 (2C), 18.65, 18.40.

IR ($CHCl_3$): 3471 w, 3386 w, 2966 s, 2868 w, 1619 m, 1605 vw, 1594 m, 1583 w, sh, 1548 w, 1496 m, 1489 s, 1475 m, sh, 1432 m, sh, 1405 vw, sh, 1396 vw, 1365 m, 1149 m, 1128 m, 1061 m, 1010 m, 878 m, 855 w, 835 w, 819 m cm^{-1}.

ESI MS: 698 ($[M+H]^+$).

HR ESI MS: calcd for $C_{50}H_{52}O_2N$ 698.3993, found 698.3993.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-12-biphenyl-4-yl-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 174d



The oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174d** was prepared according to the *General procedure B* from the chloro derivative (–)-(*M,R,R*)-**173** (99 mg, 0.15 mmol), 4-biphenylboronic acid **209** (71 mg, 0.36 mmol, 2.3 equiv.), XPhos Pd G2 (5.7 mg, 0.0072 mmol, 5 mol%) and K_3PO_4 (0.5 M in water, 0.78 ml, 0.39 mmol, 2.5 equiv.) in tetrahydrofuran (2.5 ml) at 100 °C for 1 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) gave the product (–)-(*M,R,R*)-**174d** (103 mg, 87%) as a white solid.

M.p.: 170-176 °C (hexane – acetone).

Optical rotation: $[\alpha]^{20}_D$ = -674° (c 0.252, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): 7.80 (d, *J* = 2.2, 1H), 7.63 (bs, 1H), 7.61 (m, 2H), 7.57 (m, 2H), 7.47 (dd, *J* = 8.2, 2.2, 1H), 7.43 (m, 2H), 7.37 (m, 2H), 7.33 (tt, *J* = 7.4, 1.2, 1H), 7.21 (bd, *J* = 2.3, 1H), 7.14 (m, 2H), 7.095 (d, *J* = 8.2, 1H), 7.09 (m, 2H), 7.04 (d, *J* = 8.7, 1H), 6.87 (m, 2H), 6.67 (m, 2H), 6.10 (bs, 1H), 5.29 (q, *J* = 6.7, 1H), 5.24 (q, *J* = 6.7, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.37 (s, 9H), 0.99 (d, *J* = 6.7, 3H), 0.96 (d, *J* = 6.7, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 153.13, 152.93, 149.39, 140.61, 139.58, 139.37, 139.34, 138.92, 137.38 (2C), 136.12, 136.11, 134.75, 134.72, 133.16, 131.79, 130.68, 130.63,

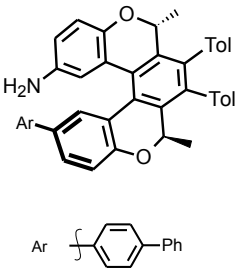
129.03, 129.00, 128.71, 128.60 (2C), 128.41, 128.39, 127.92, 127.74, 127.37, 127.16, 126.89, 126.69, 125.12, 124.96, 123.61, 123.18, 120.81, 119.84, 119.50, 119.46, 80.18, 73.14, 72.96, 28.22, 21.18 (2C), 18.53, 18.30.

IR ($CHCl_3$): 3436 w, 3028 w, 2983 m, 2868 w, 1722 s, 1601 w, 1524 s, sh, 1517 vs, 1491 w, sh, 1449 m, 1435 m, 1380 w, sh, 1368 m, 1357 vw, sh, 1256 m, 1159 vs, 1151 w, sh, 1128 vw, 1062 m, 1004 m, 910 w, 857 w, 840 w, 469 w cm^{-1}.

ESI MS: 784 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{53}H_{47}O_4NNa$ 784.3397, found 784.3402.

(–)-(*M*)-(2*R*,5*R*)-12-Biphenyl-4-yl-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c′*]dichromen-9-amine 179d



Oxa[5]helicene amine (–)-(*M,R,R*)-**179d** was prepared according to the *General procedure C* from the oxa[5]helicene derivative (–)-(*M,R,R*)-**174d** (94 mg, 0.12 mmol) and trifluoroacetic acid (240 µl, 3.1 mmol, 26 equiv.) in dichloromethane (10 ml) for 16 h. The purification by flash chromatography on silica gel (hexane-ethyl acetate 4:1) gave oxa[5]helicene amine (–)-(*M,R,R*)-**179d** (64 mg, 78%) as a yellowish solid.

M.p.: 279-283 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -742° (c 0.122, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 271 (4.69), 300 (4.44) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 496 nm.

^{1}H NMR (400 MHz, CD_2Cl_2): 7.88 (bd, *J* = 2.3, 1H), 7.66 – 7.58 (m, 4H), 7.51 – 7.42 (m, 5H), 7.37 – 7.31 (m, 1H), 7.18 – 7.10 (m, 4H), 7.08 (bd, *J* = 8.4, 1H), 6.94 – 6.91 (m, 2H), 6.87 (d, *J* = 8.6, 1H), 6.86 (d, *J* = 2.7, 1H), 6.76 – 6.72 (m, 2H), 6.63 (dd, *J* = 8.6, 2.7, 1H), 5.22 (q, *J* = 6.7, 1H), 5.12 (q, *J* = 6.7, 1H), 3.32 (s, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 0.99 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

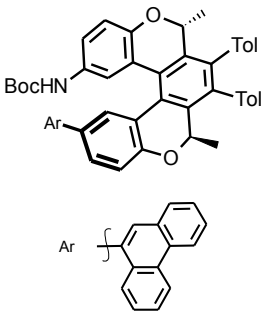
^{13}C NMR (101 MHz, CD_2Cl_2): 153.60, 146.31, 140.95 (2C), 140.20, 140.08, 139.67, 139.25, 137.74, 137.48, 136.67, 136.64, 135.48, 135.45, 133.33, 131.23, 131.17, 129.63, 129.58, 129.18, 128.86, 128.84, 128.81 (2C), 128.49, 128.00, 127.65, 127.59, 127.24, 127.19, 126.01, 125.36, 124.36, 123.81, 120.27, 119.74, 116.76, 115.76, 73.53, 72.99, 21.28 (2C), 18.71, 18.36.

IR ($CHCl_3$): 3386 w, 2985 w, 2927 w, 1619 w, 1599 w, 1547 w, 1518 w, 1495 w, sh, 1482 m, 1475 w, 1435 m, 1403 w, sh, 1331 w, 1270 w, 1150 w, 1128 w, 1107 w, 1063 w, 1005 w, 873 w, 853 w, 840 w, 699 m, 582 w, 503 w cm^{-1}.

ESI MS: 662 ($[M+H]^+$).

HR ESI MS: calcd for $C_{48}H_{40}O_2N$ 662.3054, found 662.3054.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-phenanthren-9-yl-2,5-di-hydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 174e



The oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174e** was prepared according to the *General procedure B* from the chloro derivative (–)-(*M,R,R*)-**173** (50 mg, 0.078 mmol), 9-phenanthrenylboronic acid **210** (37 mg, 0.17 mmol, 2.2 equiv.), XPhos Pd G2 (4.0 mg, 0.0051 mmol, 7 mol%) and K_3PO_4 (0.5 M in water, 0.40 ml, 0.20 mmol, 2.5 equiv.) in tetrahydrofuran (2 ml) at 100 °C for 3.5 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (–)-(*M,R,R*)-**174e** (54 mg, 89%) as a white solid.

M.p.: 197-202 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -422° (c 0.303, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): 8.74 (bd, *J* = 8.2, 1H), 8.67 (bd, *J* = 8.2, 1H), 7.91 – 7.89 (m, 1H), 7.84 – 7.82 (m, 1H), 7.68 – 7.51 (m, 6H), 7.50 (bs,1H), 7.35 (dd, *J* = 8.2, 2.1, 1H), 7.31 (bs, 1H), 7.20 – 7.14 (m, 2H), 7.12 – 7.06 (m, 3H), 6.91 – 6.85 (m, 3H), 6.71 – 6.64 (m, 2H), 6.26 (s, 1H), 5.36 (q, *J* = 6.7, 1H), 5.20 (q, *J* = 6.7, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 1.48 (s, 9H), 1.08 (d, *J* = 6.7, 3H), 0.92 (d, *J* = 6.7, 3H).

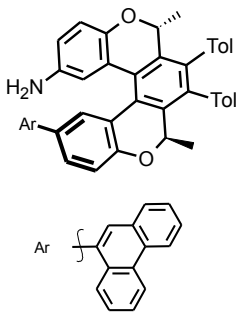
^{13}C NMR (101 MHz, $CDCl_3$): 152.94, 152.86, 149.14, 139.42, 139.10, 138.21, 137.33, 137.32, 136.12, 136.09, 134.76, 134.71, 133.48, 131.80, 131.63, 131.10, 130.95, 130.69, 130.65, 130.57, 130.53, 129.76, 129.03, 129.02, 128.64, 128.62, 128.59, 128.42, 128.38, 127.34, 126.82, 126.51, 126.43 (2C), 126.29, 125.15, 125.08, 123.65, 123.51, 122.94, 122.35, 119.81, 119.03, 118.79, 80.41, 73.22, 72.89, 28.34, 21.20, 21.17, 18.55, 18.28, one CH was not identified.

IR ($CHCl_3$): 3435 w, 2982 w, 2869 w, 1721 m, 1616 w, 1602 w, 1544 vw, sh, 1523 m, sh, 1517 m, 1496 w, 1451 w, 1435 w, 1410 w, 1393 vw, 1369 vw, 1302 w, 1279 vw, sh, 1253 m, 1184 vw, sh, 1159 m, 1150 m, sh, 1095 vw, 1061 m, 1012 w, 949 w, sh, 872 vw, 814 vw, 709 vw, sh, 590 vw, 532 w, 505 w cm^{-1}.

ESI MS: 808 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{55}H_{47}O_4NNa$ 808.3397, found 808.3399.

(–)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-12-phenanthren-9-yl-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-amine 179e



Oxa[5]helicene amine (–)-(*M,R,R*)-**179e** was prepared according to the *General procedure C* from the oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174e** (103 mg, 0.131 mmol) and trifluoroacetic acid (150 µl, 1.96 mmol, 15 equiv.) in dichloromethane (5 ml) for 16 h. The purification by flash chromatography on C-18 reversed-phase silica gel (methanol) provided oxa[5]helicene amine (–)-(*M,R,R*)-**179e** (68 mg, 76%) as a yellowish solid.

M.p.: 216-218 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -358° (c 0.322, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 253 (4.83), 302 (4.21) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 495 nm.

^{1}H NMR (400 MHz, CD_2Cl_2): 8.77 – 8.69 (m, 1H), 8.73 – 8.67 (m, 1H), 7.99 (bd, *J* = 7.8, 1H), 7.91 – 7.89 (m, 1H), 7.76 (d, *J* = 2.1, 1H), 7.74 (bs, 1H), 7.69 – 7.59 (m, 3H), 7.55 (ddd, *J* = 8.2, 6.9, 1.2, 1H), 7.38 (dd, *J* = 8.2, 2.1, 1H), 7.21 – 7.08 (m, 5H), 6.97 (bd, *J* = 2.7, 1H),

6.95 – 6.90 (m, 2H), 6.78 – 6.72 (m, 3H), 6.57 (d, J = 8.0, 1H), 5.28 (q, J = 6.7, 1H), 5.09 (q, J = 6.7, 1H), 3.45 (s, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 1.07 (d, J = 6.7, 3H), 0.91 (d, J = 6.7, 3H).

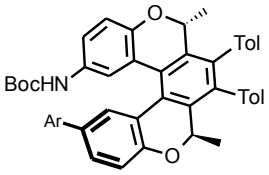
^{13}C NMR (101 MHz, CD_2Cl_2): 153.32, 146.18, 140.87, 140.13, 139.46, 138.69, 137.68, 137.47, 136.67, 136.61, 135.48, 135.47, 133.81, 132.25, 131.44, 131.26, 131.23 (2C), 131.19, 130.90, 130.10, 129.64, 129.60, 128.91, 128.87 (2C), 128.80, 128.79, 127.99, 127.18, 127.11, 126.81, 126.80, 126.72, 126.05, 125.45, 124.48, 124.10, 123.28, 122.78, 120.27, 118.97, 116.68, 115.73, 73.60, 72.95, 21.29, 21.27, 18.69, 18.35.

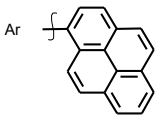
IR ($CHCl_3$): 3458 w, 3379 w, 2984 m, 1619 m, 1605 m, sh, 1589 w, sh, 1548 w, sh, 1527 w, sh, 1518 s, 1494 s, 1462 m, sh, 1450 m, 1434 m, 1405 w, 1385 m, sh, 1275 m, 1244 m, 1183 m, 1150 m, 1112 m, 1022 w, sh, 1014 m, 836 m, 821 m, 534 w cm^{-1}.

ESI MS: 686 ([M+H]$^+$).

HR ESI MS: calcd for $C_{50}H_{40}O_2N$ 686.3054, found 686.3055.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-pyren-1-yl-2,5-dihydrobenzo[1,2-*c*:4,3-*c*′]dichromen-9-yl]carbamate 174f





The oxa[5]helicene amine derivative (–)-(*M,R,R*)-**174f** was prepared according to the *General procedure B* from the chloro derivative (–)-(*M,R,R*)-**173** (100 mg, 0.156 mmol), 1-pyrenylboronic acid **211** (77 mg, 0.31 mmol, 2.1 equiv.), XPhos Pd G2 (9.1 mg, 0.012 mmol, 8 mol%) and K_3PO_4 (0.5 M in water, 0.76 ml, 0.38 mmol, 2.5 equiv.) in tetrahydrofuran (2.5 ml) at 100 °C for 3 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (–)-(*M,R,R*)-**174f** (103 mg, 82%) as a pale yellow solid.

M.p.: 180-188 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -481° (c 0.272, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): 8.18 (dd, J = 7.6, 1.1, 1H), 8.15 (dd, J = 7.7, 1.1, 1H), 8.13 (d, J = 7.8, 1H), 8.12 (d, J = 9.2, 1H), 8.065 (d, J = 9.0, 1H), 8.045 (d, J = 9.0, 1H), 8.015 (d, J

= 9.2, 1H), 8.00 (t, *J* = 7.6, 1H), 7.77 (d, *J* = 7.8, 1H), 7.73 (d, *J* = 2.1, 1H), 7.46 (bs, 1H), 7.43 (dd, *J* = 8.2, 2.1, 1H), 7.33 (bs, 1H), 7.21 (d, *J* = 8.2, 1H), 7.185 (m, 1H), 7.12 (m, 2H), 7.07 (m, 1H), 6.895 (m, 1H), 6.87 (m, 1H), 6.86 (d, *J* = 8.7, 1H), 6.69 (m, 1H), 6.66 (m, 1H), 6.19 (bs, 1H), 5.37 (q, *J* = 6.7, 1H), 5.20 (q, *J* = 6.7, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.47 (s, 9H), 1.10 (d, *J* = 6.7, 3H), 0.91 (d, *J* = 6.7, 3H).

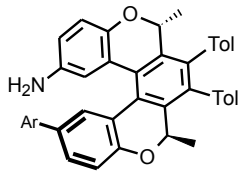
^{13}C NMR (126 MHz, $CDCl_3$): 152.97 (2C), 149.22, 139.41, 139.18, 137.36, 137.35, 136.14, 136.10, 134.76, 134.71, 134.00, 131.64, 131.52, 131.46, 130.96, 130.93, 130.70, 130.67, 130.32, 129.05, 129.01, 128.66, 128.60, 128.43, 128.39, 128.33, 127.46, 127.42, 127.38, 127.31, 127.19, 125.90, 125.18, 125.13, 125.02, 125.00, 124.92, 124.89, 124.72 (2C), 123.60, 123.56, 120.75, 119.76, 119.52, 118.95, 80.22, 73.26, 72.91, 28.35, 21.20, 21.17, 18.57, 18.28.

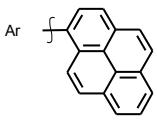
IR ($CHCl_3$): 3437 w, 2983 m, 2869 w, 1721 s, 1615 w, 1606 vw, 1587 w, 1552 w, sh, 1517 s, 1496 m, 1484 m, 1447 vw, 1416 w, 1407 w, 1393 w, 1368 m, 1299 w, 1159 s, 1123 w, 1112 vw, 1089 vw, 1060 m, 1022 w, 1003 m, 912 w, 825 w, 873 m, 712 w, 642 w, 505 w, 465 w cm^{-1}.

ESI MS: 832 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{57}H_{47}O_4NNa$ 832.3397, found 832.3403.

(–)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-12-pyren-1-yl-2,5-dihydro-benzo[1,2-*c*:4,3-*c′*]dichromen-9-amine 179f





Oxa[5]helicene amine (–)-(*M,R,R*)-**179f** was prepared according to the *General procedure C* from the oxa[5]helicene derivative (–)-(*M,R,R*)-**174f** (95 mg, 0.12 mmol) and trifluoroacetic acid (290 µl, 3.8 mmol, 33 equiv.) in dichloromethane (10 ml) for 16 h. The purification by flash chromatography on silica gel (hexane-ethyl acetate 4:1) gave oxa[5]helicene amine (–)-(*M,R,R*)-**179f** (71.5 mg, 86%) as a yellowish solid.

M.p.: 181-185 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -459° (c 0.155, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 237 (4.79), 268 (4.70), 278 (4.71), 346 (4.54) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 499 nm.

^{1}H NMR (400 MHz, CD_2Cl_2): 8.21 – 8.16 (m, 4H), 8.09 (bs, 2H), 8.04 – 7.96 (m, 3H), 7.80 (d, *J* = 2.1, 1H), 7.45 (dd, *J* = 8.1, 2.1, 1H), 7.20 (d, *J* = 8.1, 1H), 7.20 – 7.09 (m, 4H), 6.97 (d, *J* = 2.7, 1H), 6.95 – 6.90 (m, 2H), 6.78 – 6.72 (m, 2H), 6.70 (bd, *J* = 8.5, 1H), 6.47 (dd, *J* = 8.5, 2.7, 1H), 5.30 (q, *J* = 6.6, 1H), 5.08 (q, *J* = 6.6, 1H), 3.39 (s, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 1.09 (d, *J* = 6.6, 3H), 0.90 (d, *J* = 6.6, 3H).

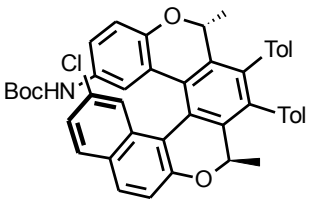
^{13}C NMR (101 MHz, CD_2Cl_2): 153.40, 146.10, 140.88, 140.11, 139.55, 137.99, 137.72, 137.48, 136.69, 136.62, 135.48, 135.47, 134.26, 131.87, 131.80, 131.59, 131.38, 131.27, 131.20, 130.73, 129.63, 129.62, 128.88 (2C), 128.81, 128.80, 128.78, 128.19, 127.77, 127.59, 127.56, 126.38, 126.11, 125.65, 125.46, 125.39, 125.22, 125.21, 125.13, 124.97, 124.37, 124.17, 120.17, 119.23, 116.68, 115.69, 73.65, 72.94, 21.30, 21.27, 18.71, 18.35.

IR ($CHCl_3$): 3468 w, 3383 w, 1619 w, 1603 vw, sh, 1596 vw, sh, 1583 vw, 1544 w, 1518 m, 1494 m, 1484 m, 1456 m, 1431 m, 1367 m, 1333 vw, 1262 m, 1184 w, 1150 m, 1128 w, 1062 m, 1009 vw, sh, 880 w, 850 m, 843 vw, 836 vw, sh, 819 m cm^{-1}.

ESI MS: 710 ($[M+H]^+$).

HR ESI MS: calcd for $C_{52}H_{40}O_2N$ 710.3054, found.710.3055.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-11-chloro-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[*f*]benzo[1,2-*c*:4,3-*c*']dichromen-14-yl]carbamate 181



Oxa[6]helicene (–)-(*M,R,R*)-**181** was prepared according to the *General procedure A* from triyne (–)-(*R,R*)-**192** (121 mg, 0.174 mmol), CpCo(CO)(fum) (22 mg, 0.074 mmol, 43 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (33 mg) in tetrahydrofuran (5 ml). The purification by flash chromatography on silica gel (hexane–ethyl acetate 15:1) and then on C-18 reversed-phase silica gel (methanol) gave the cyclic product (–)-(*M,R,R*)-**181** (84 mg, 70%) as a pale yellow solid.

M.p.: 184.9 – 186.9 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -667° (c 0.145, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 7.71 (d, *J* = 8.7, 1H), 7.59 (d, *J* = 8.6, 1H), 7.47 (d, *J* = 1.8, 1H), 7.26 (d, *J* = 8.7, 1H), 7.19 – 7.14 (m, 2H), 7.11 (dd, *J* = 8.6, 1.8, 1H), 7.10 (bs, 1H), 7.11– 7.07 (m, 2H), 6.93 (d, *J* = 8.6, 1H), 6.93 – 6.89 (m, 2H), 6.78 – 6.73 (m, 2H), 6.27 (bs, 1H), 5.44 (bs, 1H), 5.33 (q, *J* = 6.7, 1H), 5.28 (q, *J* = 6.7, 1H), 2.28 (bs, 6H), 1.40 (s, 9H), 1.01 (d, *J* = 6.7, 3H), 0.99 (d, *J* = 6.7, 3H).

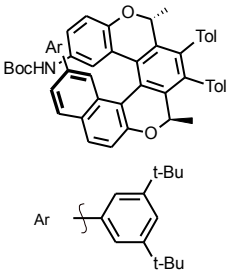
^{13}C NMR (151 MHz, $CDCl_3$): 153.72, 149.10, 139.46, 138.93, 137.16, 136.97, 136.16, 136.12, 134.83 (2C), 131.89, 131.35, 130.78, 130.51, 130.18, 129.85, 129.11, 129.01, 128.84, 128.64, 128.48, 128.46, 128.37, 128.09, 125.67, 125.08, 124.36, 123.83, 123.22, 120.38, 119.96, 118.70, 118.25, 117.36, 79.85, 73.53, 72.94, 28.24, 21.19 (2C), 18.60, 17.81. Quaternary carbon from carbamate was not found.

IR ($CHCl_3$): 3414 m, 3348 m, 2979 m, 2927 m, 2868 w, 1727 s, 1615 m, 1596 w, 1518 s, 1503 m, 1493 m, 1391 m, 1368 m, 1222 m, 1160 s, 1073 m, 757 m cm^{-1}.

ESI MS: 716 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{45}H_{40}O_4N^{35}ClNa$ 716.2538, found 716.2541.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-11-(3,5-di-*t*ert-butylphenyl)-2,5-dimethyl-3,4-bis(4-methyl-phenyl)-2,5-dihydrobenzo[*f*]benzo[1,2-*c*:4,3-*c*']dichromen-14-yl]carbamate 193



Oxa[6]helicene (–)-(*M,R,R*)-**193** was prepared according to the *General procedure B* from chlorooxa[6]helicene (–)-(*M,R,R*)-**181** (80 mg, 0.12 mmol), 3,5-di-*tert*-butylphenyl boronic acid **215**[169] (53 mg, 0.23 mmol, 2.0 equiv.), XPhos Pd G2 (9.0 mg, 0.011 mmol, 10 mol%) and K_3PO_4 (0.5 M in water, 0.58 ml, 0.29 mmol, 2.5 equiv.) in distilled toluene (2.5 ml) at 120 °C for 2 h. The purification by flash chromatography on silica gel (hexane–acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (–)-(*M,R,R*)-**193** (85 mg, 86%) as a pale yellow solid.

M.p.: 174.3-176.4 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -691° (c 0.339, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 7.79 (d, *J* = 8.6, 1H), 7.78 (d, *J* = 8.6, 1H), 7.74 (bs, 1H), 7.44 (dd, *J* = 8.6, 1.6, 1H), 7.36 (t, *J* = 1.7, 1H), 7.28 (d, *J* = 8.6, 1H), 7.19 – 7.16 (m, 1H), 7.14 (bs, 1H), 7.12 (d, *J* = 1.7, 2H), 7.10 – 7.07 (m, 3H), 6.92 – 7.07 (m, 3H), 6.79 (m, 1H), 6.71 (m, 1H), 6.30 (bs, 1H), 5.38 (s, 1H), 5.31 (q, *J* = 6.6, 1H), 5.25 (q, *J* = 6.6, 1H), 2.27 (s, 6H), 1.40 (s, 9H), 1.37 (s, 18H), 1.02 (d, *J* = 6.6, 3H), 0.95 (d, *J* = 6.6, 3H).

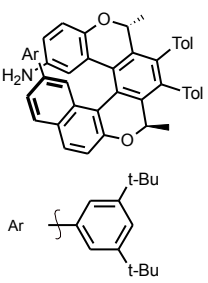
^{13}C NMR (151 MHz, $CDCl_3$): 153.16, 152.64, 150.92, 148.78, 140.80, 140.22, 139.62, 138.62, 137.14, 136.71, 136.06, 135.96, 135.07, 134.96, 131.31, 130.93, 130.51, 130.10, 129.75, 129.16, 129.00, 128.84, 125.58, 128.47, 128.39, 128.30, 128.03, 125.66, 124.22, 124.10, 123.96, 123.80, 122.25, 121.02, 120.07, 119.49, 119.06 (2C), 118.30, 79.86, 73.52, 72.65, 34.96, 31.55, 28.25, 21.19, 21.17, 18.88, 17.61.

IR ($CHCl_3$): 3440 w, 2986 m, sh, 2966 m, 2929 m, 2868 w, 1723 m, 1619 m, 1608 w, sh, 1597 m, 1569 w, 1547 w, sh, 1517 s, 1494 m, 1478 w, 1426 m, 1393 w, 1368 m, 1160 s, 1123 w, 1017 m, 923 w, 838 m, 812 m, 643 w, 541 w, 500 w cm^{-1}.

ESI MS: 870 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{59}H_{61}O_4NNa$ 870.4493, found 870.4495.

(–)-(*M*)-(2*R*,5*R*)-11-(3,5-di-*tert*-Butylphenyl)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[*f*]benzo[1,2-*c*:4,3-*c*']dichromen-14-amine 194



Aminooxa[6]helicene (–)-(*M,R,R*)-**194** was prepared according to the *General procedure C* from oxa[6]helicene (–)-(*M,R,R*)-**193** (60.6 mg, 0.0715 mmol) and trifluoroacetic acid (110 µl, 1.44 mmol, 20.0 equiv.) in dichloromethane (3 ml) for 16 h. The purification by flash chromatography on silica gel (hexane–ethyl acetate 5:1) gave oxa[6]helicene amine (–)-(*M,R,R*)-**194** (43 mg, 81%) as a yellowish solid.

M.p.: 172.1-174.4 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -704° (c 0.105, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 212 (5.29), 261 (5.17), 337 (4.41), 362 (4.43), 418 (3.06) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 360 nm): λ_{max} = 541 nm.

^{1}H NMR (600 MHz, CD_2Cl_2): 7.81 (dd, *J* = 8.6, 0.8, 1H), 7.79 (bd, *J* = 8.4, 1H), 7.77 (dt, *J* = 1.8, 0.8, 1H), 7.46 (dd, *J* = 8.4, 1.8, 1H), 7.36 (t, *J* = 1.8, 1H), 7.27 (d, *J* = 8.6, 1H), 7.20 (m, 1H), 7.17 (d, *J* = 1.8, 2H), 7.14 (m, 1H), 7.12 (m, 2H), 6.96 – 6.92 (m, 2H), 6.85 (m, 1H), 6.76 (m, 1H), 6.73 (d, *J* = 8.4, 1H), 6.25 (dd, *J* = 8.4, 2.7, 1H), 5.89 (d, *J* = 2.7, 1H), 5.25 (q, *J* = 6.7, 1H), 5.17 (q, *J* = 6.7, 1H), 2.74 (bs, 2H), 2.28 (s, 6H), 1.37 (s, 18H), 1.00 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

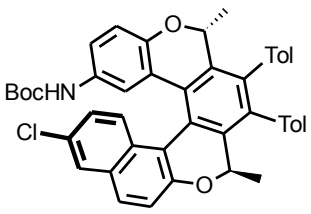
^{13}C NMR (151 MHz, CD_2Cl_2): 153.47, 151.45, 145.69, 141.00, 140.64, 140.17, 140.08, 139.37, 137.30, 137.10, 136.67, 136.55, 135.76, 135.61, 131.48, 131.07, 130.70, 129.94, 129.74, 129.58, 129.41, 128.88, 128.86, 128.77, 128.67, 128.48, 126.71, 124.82, 124.28, 124.21, 124.10, 122.41, 121.41, 119.84, 119.68, 119.05, 115.89, 115.17, 73.96, 72.76, 35.28, 31.70, 21.29, 21.28, 18.90, 17.81.

IR ($CHCl_3$): 3054 w, 2966 vs, 1619 m, 1541 w, 1517 m, 1493 m, 1430 m, 1404 w, sh, 1394 m, 1385 w, 1367 m, 1353 m, sh, 1277 w, 1184 m, 1123 w, 1111 w, 1028 m, 839 m, 811 m, 693 w, 521 w cm^{-1}.

ESI MS: 748 ($[M+H]^+$).

HR ESI MS: calcd for $C_{54}H_{54}O_2N$ 748.4149, found 748.4152.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-10-chloro-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[*f*]benzo[1,2-*c*:4,3-*c'*]dichromen-14-yl]carbamate 182



Oxa[6]helicene (–)-(*M,R,R*)-**182** was prepared according to the *General procedure A* from triyne (–)-(*R,R*)-**204** (95 mg, 0.14 mmol), CpCo(CO)(fum) (19 mg, 0.064 mmol, 47 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (33 mg) in tetrahydrofuran (5 ml). The purification by flash chromatography on silica gel (hexane–ethyl acetate 10:1) and then on C-18 reversed-phase silica gel (methanol) gave the cyclic product (–)-(*M,R,R*)-**182** (78 mg, 82%) as a pale yellow solid.

M.p.:179.0-181.4 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -620° (c 0.197, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 7.65 (d, *J* = 8.7, 1H), 7.64 (d, *J* = 2.3, 1H), 7.44 (d, *J* = 9.1, 1H), 7.29 (d, *J* = 8.7, 1H), 7.155 (m, 1H), 7.15 (m, 1H), 7.12 – 7.02 (m, 2H), 7.10 (bd, *J* = 8.6, 1H), 6.90 – 6.86 (m, 2H), 6.89 (d, *J* = 8.6, 1H), 6.88 (dd, *J* = 9.1, 2.3, 1H), 6.76 (m, 1H), 6.74 (m, 1H), 6.26 (bs, 1H), 5.49 (s, 1H), 5.32 (q, *J* = 6.7, 1H), 5.27 (q, *J* = 6.7, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 1.41 (s, 9H), 1.00 (d, *J* = 6.7, 3H), 0.96 (d, *J* = 6.7, 3H).

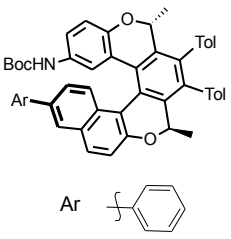
^{13}C NMR (151 MHz, $CDCl_3$): 152.99, 148.49, 139.66, 138.77, 137.20, 136.98, 136.18, 136.14, 134.80, 134.78, 131.67, 130.82, 130.65, 130.45, 129.13 (2C), 129.08, 128.92, 128.64, 128.52, 128.47, 128.37, 127.77, 127.23, 126.15, 125.82, 125.80, 123.98, 123.39, 120.96, 120.17, 118.88, 118.71, 118.14, 79.98, 73.46, 73.00, 28.23, 21.18 (2C), 18.60, 17.77. Quaternary carbon from carbamate was not found.

IR ($CHCl_3$): 3448 m, 3348 m, 2997 m, 2978 m, 2867 w, 1727 s, 1617 m, 1589 m, 1517 s, 1493 m, 1442 m, 1395 m, 1367 m, 1224 m, 1160 s, 1074 m, 755 m cm^{-1}.

ESI MS: 716 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{45}H_{40}O_4N^{35}ClNa$ 716.2538, found 716.2540.

(–)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-10-phenyl-2,5-dihydrobenzo[*f*]benzo[1,2-*c*:4,3-*c*']dichromen-14-yl]carbamate 205



Oxa[6]helicene (–)-(*M,R,R*)-**205** was prepared according to the *General procedure B* from chlorooxa[6]helicene (–)-(*M,R,R*)-**182** (42 mg, 0.060 mmol), phenyl boronic acid **212** (20.5 mg, 0.168 mmol, 2.8 equiv.), XPhos Pd G2 (4.6 mg, 0.0058 mmol, 10 mol%) and K_3PO_4 (0.5 M in water, 300 µl, 0.15 mmol, 2.5 equiv.) in tetrahydrofuran (1.5 ml) at 100 °C for 3 h. The purification by flash chromatography on silica gel (hexane – acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (–)-(*M,R,R*)-**205** (43 mg, 96%) as an off- white solid.

M.p.:162.8-164.7 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -621° (c 0.207, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 7.88 (d, *J* = 2.0, 1H), 7.81 (bd, *J* = 8.6, 1H), 7.60 (m, 2H), 7.54 (bd, *J* = 8.7, 1H), 7.44 (m, 2H), 7.34 (m, 1H), 7.30 (d, *J* = 8.6, 1H), 7.21 (dd, *J* = 8.7, 2.0, 1H), 7.14 – 7.08 (m, 4H), 7.16 (bs, 1H), 6.91 (m, 2H), 6.89 (d, *J* = 8.6, 1H), 6.77 (m, 2H), 6.22 (d, *J* = 2.6, 1H), 5.34 (q, *J* = 6.6, 1H), 5.29 (q, *J* = 6.6, 1H), 5.31 (s, 1H), 2.28 (s, 6H), 1.34 (s, 9H), 1.019 (d, *J* = 6.6, 3H), 1.017 (d, *J* = 6.6, 3H).

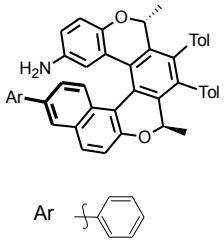
^{13}C NMR (151 MHz, $CDCl_3$): 153.01, 152.51, 148.56, 141.01, 139.52, 138.68, 137.17, 136.80, 136.12 (2C), 136.08, 134.93 (2C), 131.61, 130.86, 130.50, 130.42, 130.14, 129.18, 128.99, 128.71, 128.68, 128.61, 128.49, 128.45, 128.36, 127.16, 127.02, 126.15, 125.72, 125.29, 124.69, 124.10, 123.76, 120.18, 119.92, 119.05, 118.54, 117.83, 79.77, 73.44, 72.99, 26.18, 21.19 (2C), 18.62, 17.80.

IR ($CHCl_3$): 3440 w, 2982 m, 2928 w, 2868 w, 1722 m, 1617 w, 1593 m, 1547 w, sh, 1517 s, 1493 s, 1445 w, 1407 w, 1389 w, 1369 m, 1301 w, sh, 1271 w, 1254 m, 1183 m, 1160 s, 1015 m, 857 w, 824 m, 814 w, 555 w, 533 w, 433 vw, sh cm^{-1}.

ESI MS: 758 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{51}H_{45}O_4NNa$ 758.3241, found 758.3242.

(–)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-10-phenyl-2,5-dihydrobenzo-[*f*]benzo[1,2-*c*:4,3-*c*']dichromen-14-amine 206



Aminooxa[6]helicene (–)-(*M,R,R*)-**206** was prepared according to the *General procedure C* from oxa[6]helicene (–)-(*M,R,R*)-**205** (46 mg, 0.063 mmol) and trifluoroacetic acid (100 µl, 1.31 mol, 21.0 equiv.) in dichloromethane (5 ml) for 16 h. Evaporation of solvent provided oxa[6]helicene amine (–)-(*M,R,R*)-**206** (35.4 mg, 91%) as a yellowish solid.

M.p.: 185.3-189.1 °C (dichloromethane).

Optical rotation: $[\alpha]^{20}_D$ = -864.2° (c 0.135, CH_2Cl_2).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 273 (5.11), 369 (4.32), 420 (3.22) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 370 nm): λ_{max} = 536 nm.

^{1}H NMR (400 MHz, CD_2Cl_2): 7.94 (d, *J* = 1.9, 1H), 7.85 (bd, *J* = 8.5, 1H), 7.66 – 7.62 (m, 2H), 7.58 (bd, *J* = 8.9, 1H), 7.48 – 7.42 (m, 2H), 7.37 – 7.27 (m, 2H), 7.31 (d, *J* = 8.7, 1H), 7.22 – 7.12 (m, 4H), 6.98 – 6.93 (m, 2H), 6.86 – 6.81 (m, 2H), 6.72 (d, *J* = 8.4, 1H), 6.26 (dd, *J* = 8.4, 2.7, 1H), 5.83 (d, *J* = 2.7, 1H), 5.27 (q, *J* = 6.7, 1H), 5.16 (q, *J* = 6.7, 1H), 2.69 (s, 2H), 2.29 (s, 6H), 1.00 (d, *J* = 6.7, 3H), 0.98 (d, *J* = 6.7, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): 153.32, 145.61, 141.14, 140.87, 140.08, 139.42, 137.29, 137.17, 136.71, 136.63, 136.10, 135.65, 135.59, 131.40, 131.08, 130.71, 130.67, 129.73, 129.57, 129.30, 129.20, 128.88, 128.87, 128.81, 128.74, 127.51, 127.26, 126.84, 126.57, 125.64, 124.97, 124.80, 124.02, 120.54, 119.13, 118.64, 115.87, 115.21, 73.91, 72.98, 21.30 (2C), 18.70. 17.98.

IR ($CHCl_3$): 3361 w, 3086 w, 3032 w, 3050 w, sh, 1619 w, 1592 m, 1575 w, 1543 w, 1517 m, 1492 s, 1403 m, sh, 1374 w, 1368 w, 1339 w, 1305 w, 1275 w, sh, 1184 m, 1122 w, 1111 m, 1077 m, 1022 m, 844 m, 821 m, 811 m, 699 m, 690 w, sh, 642 w, 553 w cm^{-1}.

ESI MS: 636 ($[M+H]^+$).

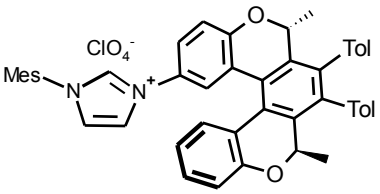
HR ESI MS: calcd for $C_{46}H_{38}O_2N$ 636.2897, found 636.2898

Synthesis of oxahelicene imidazolium (–)-(*M,R,R*),(*M,R,R*)-136a, **(–)-(*M,R,R*),(*M,R,R*)-137a**, **(–)-(*M,R*),(*M,R*)-162**, **(–)-(*M,R*),(*M,R*)-163**, **(–)-(*M,R,R*),(*M,R,R*)-180a-f (–)-(*M,R,R*),(*M,R,R*)-207**, **and (–)-(*M,R,R*),(*M,R,R*)-208**.

General procedure D *(preparation of symmetrical imidazolium chlorides*[150]*)*: The reaction was performed in an open vessel under ambient atmosphere. A solution of glyoxal (40 wt% in H_2O, 0.5 – 0.6 equiv.), formaldehyde (37 wt% in H_2O, 0.6 – 0.8 equiv.) and acetic acid (0.5 ml) was heated at 40 - 55 °C for 5 min before it was added to a solution of oxahelicene amine (–)-(*M,R,R*)-**134**, (–)-(*M,R,R*)-**135**, (–)-(*M,R*)-**166**, (–)-(*M,R*)-**167**, (–)-(*M,R,R*)-**179a-f**, (–)-(*M,R,R*)-**194** or (–)-(*M,R,R*)-**206** (1.0 equiv.) in acetic acid (0.5 ml), which was also pre-heated at 40-55 °C for 5 min. The resulting mixture was stirred at 40 - 55 °C for 25 min. - 3.7 h. Then the reaction mixture was cooled down to room temperature. Dichloromethane (10 ml) was added and the organic layer was successively washed with water (10 ml), brine (3 × 10 ml) and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel to afford the desired imidazolium

chloride (–)-(*M,R,R*),(*M,R,R*)-**136a**, (–)-(*M,R,R*),(*M,R,R*)-**137a**, (–)-(*M,R*),(*M,R*)-**162**, (–)-(*M,R*),(*M,R*)-**163**, (–)-(*M,R,R*),(*M,R,R*)-**180a-f**, (–)-(*M,R,R*),(*M,R,R*)-**207**, and (–)-(*M,R,R*),(*M,R,R*)-**208**.

(–)-(*M*)-1-[(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c′*]dichro-men-9-yl]-3-(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium perchlorate 138a



A suspension of oxazolinium perchlorate **157** (freshly prepared from *N*-mesityl-*N*-(2-oxoethyl)formamide **158** (38 mg, 0.19 mmol, 1.9 equiv.), acetic anhydride (180 µl) and $HClO_4$ (70 wt%, 30 µl, 0.35 mmol, 3.6 equiv.) according to the literature procedure[151]) in toluene (1.5 ml) was reacted with oxa[5]helicene amine (–)-(*M,R,R*)-**134** (49 mg, 0.10 mmol) at room temperature for 4 h and then $HClO_4$ (70 wt%, 30 µl, 0.35 mmol, 3.6 equiv.) was added. The mixture was stirred at 80 °C for 16 h, then the solvent was removed *in vacuo*. The crude product was flash chromatographed on silica gel (dichloromethane-acetonitrile 20:1 then dichloromethane-methanol 20:1) to provide (–)-(*M,R,R*)-**138a** (29 mg, 38%) as a brown solid.

M.p.: 206-209 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_D$ = -452° (c 0.215, $CHCl_3$).

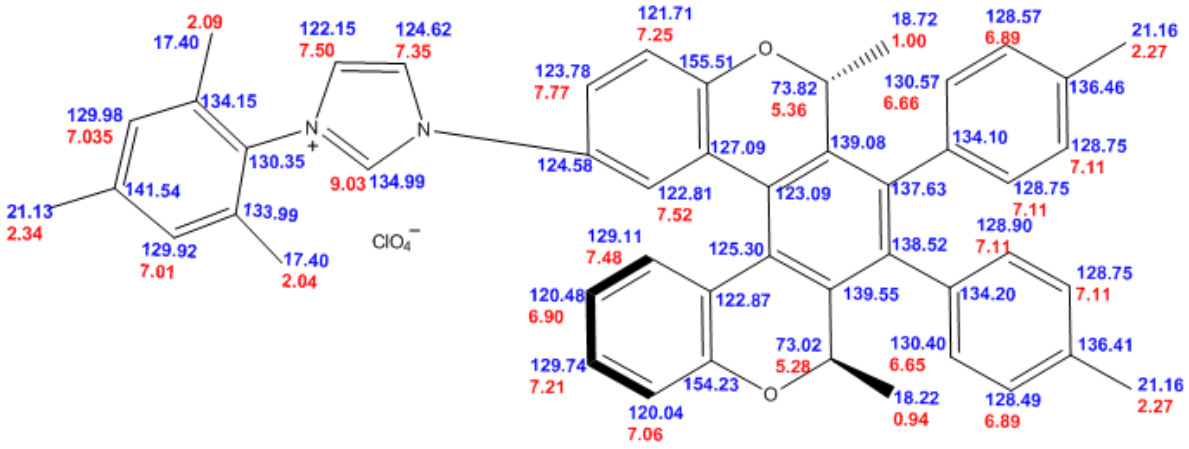
UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 263 (4.55), 337 (4.04) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 408 nm.

^{1}H NMR (500 MHz, $CDCl_3$): 9.03 (t, *J* = 1.6, 1H), 7.77 (dd, *J* = 8.7, 2.8, 1H), 7.52 (d, *J* = 2.8, 1H), 7.50 (dd, *J* = 1.8, 1.6, 1H), 7.48 (dd, *J* = 7.8, 1.6, 1H), 7.35 (dd, *J* = 1.8, 1.6, 1H), 7.25 (d, *J* = 8.7, 1H), 7.21 (ddd, *J* = 8.1, 7.3, 1.6, 1H), 7.11 (m, 4H), 7.06 (dd, *J* = 8.1, 1.2, 1H), 7.035 (bs, 1H), 7.01 (bs, 1H), 6.90 (ddd, *J* = 7.8, 7.3, 1.2, 1H), 6.89 (m, 2H), 6.66 (m, 1H), 6.65 (m, 1H), 5.36 (q, *J* = 6.7, 1H), 5.28 (q, *J* = 6.7, 1H), 2.34 (s, 3H), 2.27 (s, 6H), 2.09 (s, 3H), 2.04 (s, 3H), 1.00 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 155.51, 154.23, 141.54, 139.55, 139.08, 138.52, 137.63, 136.46, 136.41, 134.99, 134.20, 134.15, 134.10, 133.99, 130.57, 130.40, 130.35, 129.98, 129.92, 129.74, 129.11, 128.80, 128.75 (3C), 128.57, 128.49, 127.09, 125.30, 124.62,

124.58, 123.78, 123.09, 122.87, 122.81, 122.15, 121.71, 120.48, 120.04, 73.82, 73.02, 21.16 (2C), 21.13, 18.72, 18.22, 17.40.

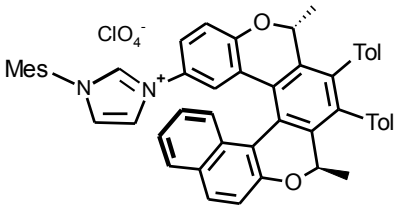


IR ($CHCl_3$): 3164 w, 3140 w, 3053 w, sh, 2983 m, 1612 w, sh, 1603 w, 1593 vw, 1583 w, 1541 m, 1518 m, 1495 m, sh, 1485 m, 1448 m, 1425 m, 1404 vw, 1379 m, sh, 1369 m, 1183 w, 1147 s, 1127 s, 1106 vs, 1099 vs, 1033 m, 1022 m, 981 w, 947 vw, 886 w, 855 m, 838 m, 819 w, 635 m, 627 m, 576 w, 534 w, 521 w, 461 w cm^{-1}.

ESI MS: 679 ($[M]^+$).

HR ESI MS: calcd for $C_{48}H_{43}O_2N_2$ 679.3319, found 679.3317.

(–)-(*M*)-1-[(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[*f*]benzo-[1,2-*c*:4,3-*c′*]dichro-men-14-yl]-3-(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium-perchlorate 139a



A suspension of oxazolinium perchlorate **157** (freshly prepared from *N*-mesityl-*N*-(2-oxoethyl)formamide **158** (72 mg, 0.35 mmol, 2.1 equiv.), acetic anhydride (400 µl) and $HClO_4$ (70 wt%, 30 µl, 0.37 mmol, 2.2 equiv.) according to the literature procedure[151]) in toluene (2.3 ml) was reacted with oxa[6]helicene amine (–)-(*M,R,R*)-**135** (93 mg, 0.17 mmol) at room temperature for 4 h and then $HClO_4$ (70 wt%, 30 µl, 0.37 mmol, 2.2 equiv.) was added. The mixture was stirred at 80 °C for 16 h, then the solvent was removed *in vacuo*. The crude product was flash chromatographed on silica gel

(dichloromethane–acetonitrile 20:1 then dichloromethane–methanol 20:1) to provide (–)-(*M,R,R*)-**139a** (38 mg, 28%) as a brown solid.

M.p.:199.8-201.5 °C (dichloromethane – methanol).

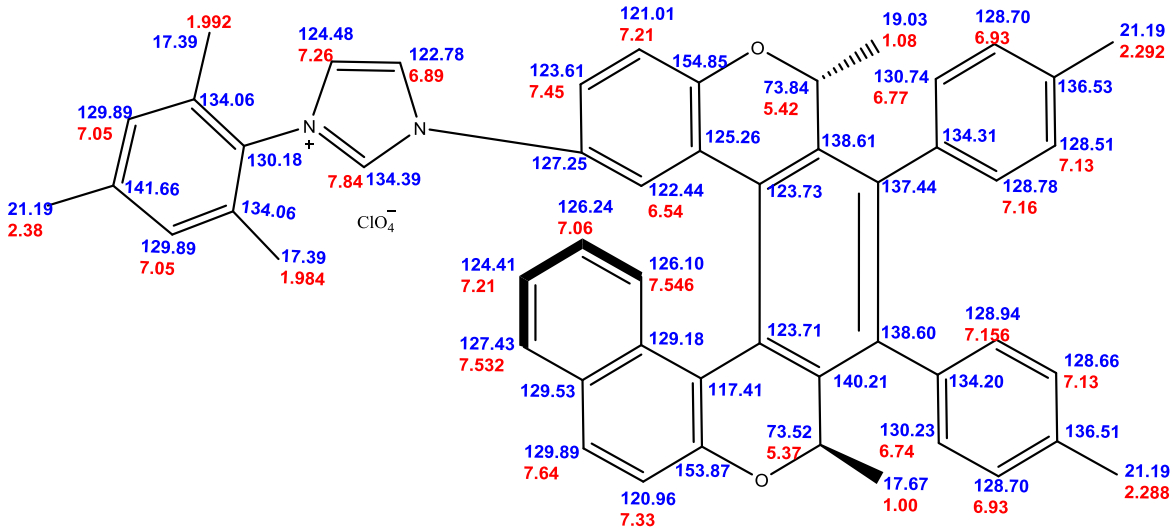
Optical rotation: $[\alpha]^{20}_{D}$ = -388° (c 0.100, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 235 (5.08), 313 (4.53), 342 (4.38) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 433 nm.

^{1}H NMR (500 MHz, $CDCl_3$): 7.84 (s, 1H), 7.64 (d, *J* = 8.7, 1H), 7.546 (bd, *J* = 8.5, 1H), 7.532 (bd, *J* = 8.2, 1H), 7.45 (dd, *J* = 8.7, 2.7, 1H), 7.33 (d, *J* = 8.7, 1H), 7.26 (m, 1H), 7.21 (bd, *J* = 8.7, 1H), 7.21 (ddd, *J* = 8.5, 6.8, 1.1, 1H), 7.18 – 7.10 (m, 4H), 7.06 (ddd, *J* = 8.5, 6.8, 1.3, 1H), 7.05 (m, 2H), 6.93 (m, 2H), 6.89 (m, 1H), 6.77 (m, 1H), 6.74 (m, 1H), 6.54 (d, *J* = 2.7, 1H), 5.42 (q, *J* = 6.7, 1H), 5.37 (q, *J* = 6.7, 1H), 2.38 (s, 3H), 2.292 (s, 3H), 2.288 (s, 3H), 1.992 (s, 3H), 1.984 (s, 3H), 1.08 (d, *J* = 6.7, 3H), 1.00 (d, *J* = 6.7, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 154.85, 153.87, 141.66, 140.21, 138.61, 138.60, 137.44, 136.53, 136.51, 134.39, 134.31, 134.20, 134.06, 130.74, 130.23, 130.18, 129.89 (2C), 129.53, 129.18, 128.94, 128.78, 128.70 (2C), 128.66, 128.51, 127.43, 127.25, 126.24, 126.10, 125.26, 124.48, 124.41, 123.73, 123.71, 123.61, 122.78, 122.44, 121.01, 120.96, 117.41, 73.84, 73.52, 21.19 (3C), 19.03, 17.67, 17.39.



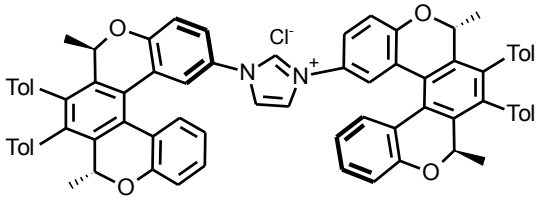
IR ($CHCl_3$): 3164 w, 2928 s, 1736 w, 1616 m, sh, 1602 w, 1592 m, 1544 m, 1517 w, 1509 w, 1489 m, 1143 w, 1426 vw, sh, 1404 w, sh, 1380 m, 1370 m, 1182 m, 1153 m, 1129 s,

1107 s, 1077 s, 1064 m, sh, 1017 w, 1032 w, 981 w, 940 w, sh, 885 w, 854 w, sh, 838 m, 625 m, 579 w, 527w cm^{-1}.

ESI MS: 729 ($[M]^+$).

HR ESI MS: calcd for $C_{52}H_{45}O_2N_2$ 729.3476, found 729.3479.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[1,2-*c*:4,3-*c′*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 136a



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**136a** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M,R,R*)-**134** (100 mg, 0.20 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 11 µl, 0.096 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 10 µl, 0.13 mmol, 0.7 equiv.) in acetic acid (0.5 ml) at 40 °C for 25 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**136a** (70 mg, 66%) as a pale white solid.

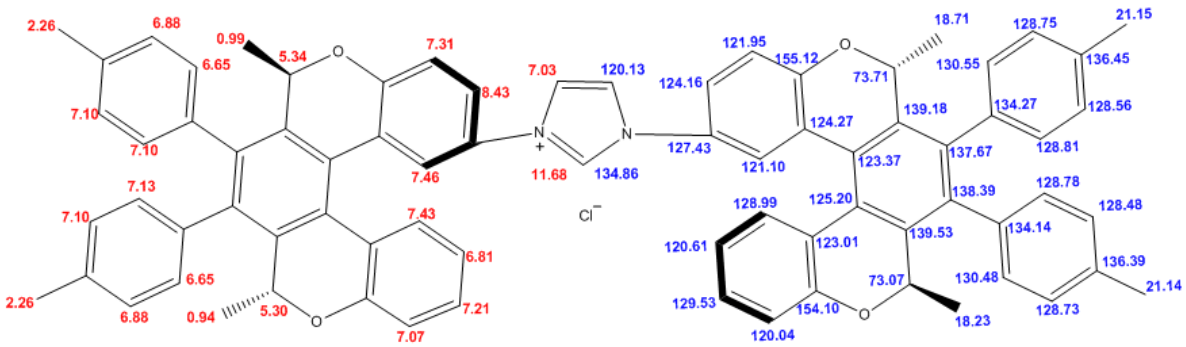
M.p.: 238-242 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_D$ = -601° (c 0.091, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 270 (4.95), 336 (4.44) nm.

^{1}H NMR (600 MHz, $CDCl_3$): 11.68 (t, *J* = 1.6, 1H), 8.43 (dd, *J* = 8.8, 2.8, 2H), 7.46 (d, *J* = 2.8, 2H), 7.43 (dd, *J* = 7.9, 1.6, 2H), 7.31 (d, *J* = 8.8, 2H), 7.21 (ddd, *J* = 8.0, 7.3, 1.6, 2H), 7.13 (m, 2H), 7.11 – 7.09 (m, 6H), 7.07 (dd, *J* = 8.0, 1.3, 2H), 7.03 (d, *J* = 1.6, 2H), 6.88 (m, 4H), 6.81 (ddd, *J* = 7.9, 7.3, 1.3, 2H), 6.66 – 6.64 (m, 4H), 5.34 (q, *J* = 6.7, 2H), 5.30 (q, *J* = 6.7, 2H), 2.26 (bs, 12H), 0.99 (d, *J* = 6.7, 6H), 0.94 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 155.12, 154.10, 139.53, 139.18, 138.39, 137.67, 136.45, 136.39, 134.86, 134.27, 134.14, 130.55, 130.48, 129.53, 128.99, 128.81, 128.78, 128.75, 128.73, 128.56, 128.48, 127.43, 125.20, 124.27, 124.16, 123.37, 123.01, 121.95, 121.10, 120.61, 120.13, 120.04, 73.71, 73.07, 21.15, 21.14, 18.71, 18.23.

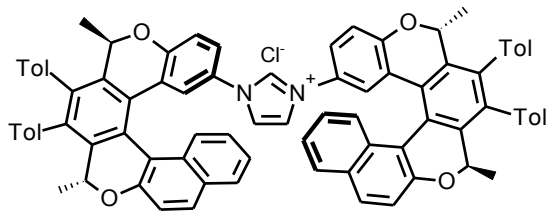


IR (KBr): 3145 w, 3050 m, 2980 m, 1603 m, 1583 m, 1517 s, 1485 s, 1446 s, 1405 w, 1183 w, 1149 m, 1111 m, 1022 m, 980 w, 886 w, 837 m, 761 m cm^{-1}.

ESI MS: 1053 ($[M]^+$).

HR ESI MS: calcd for $C_{75}H_{61}O_4N_2$ 1053.4626, found 1053.4626.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[*f*]benzo-[1,2-*c*:4,3-*c*′]dichromen-14-yl]-1*H*-imidazol-3-ium chloride 137a



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**137a** was synthesised according to the *General procedure D* from oxa[6]helicene amine (–)-(*M,R,R*)-**135** (47 mg, 0.084 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 55 °C for 35 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**137a** (39 mg, 78%) as a pale white solid.

M.p.: 288-294 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_D$ = -669° (c 0.247, $CHCl_3$).

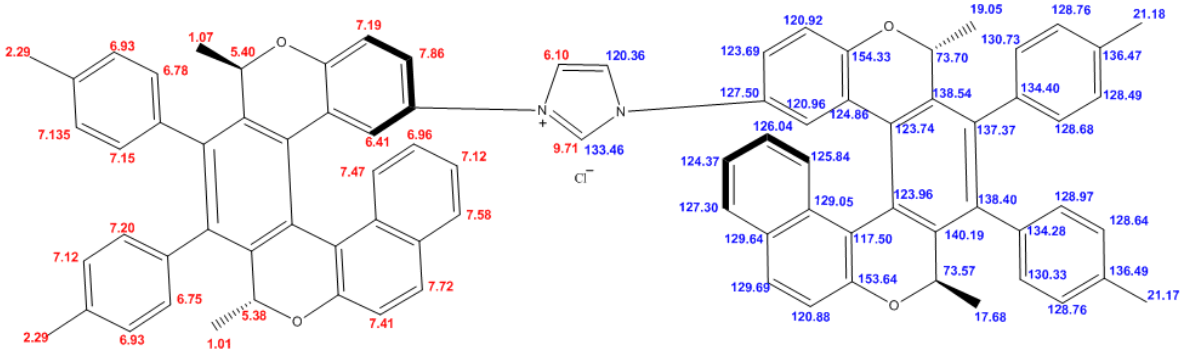
UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 241 (4.77), 259 (5.69), 351 (4.09) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 432 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 9.71 (t, *J* = 1.6, 1H), 7.86 (dd, *J* = 8.7, 2.8, 2H), 7.72 (d, *J* = 8.6, 2H), 7.58 (bdd, *J* = 8.2, 1.2, 2H), 7.47 (dd, *J* = 8.6, 1.0, 2H), 7.41 (d, *J* = 8.6, 2H), 7.20

(m, 2H), 7.19 (d, *J* = 8.7, 2H), 7.15 (m, 2H), 7.135 (m, 2H), 7.12 (m, 2H), 7.12 (ddd, *J* = 8.2, 6.8, 1.0, 2H), 6.96 (ddd, *J* = 8.6, 6.8, 1.2, 2H), 6.93 (m, 4H), 6.78 (m, 2H), 6.75 (m, 2H), 6.41 (d, *J* = 2.8, 2H), 6.10 (d, *J* = 1.6, 2H), 5.40 (q, *J* = 6.7, 2H), 5.38 (q, *J* = 6.7, 2H), 2.29 (s, 12H), 1.07 (d, *J* = 6.7, 6H), 1.01 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 154.33, 153.64, 140.19, 138.54, 138.40, 137.37, 136.49, 136.47, 134.40, 134.28, 133.46, 130.73, 130.33, 129.69, 129.64, 129.05, 128.97, 128.76 (2C), 128.68, 128.64, 128.49, 127.50, 127.30, 126.04, 125.84, 124.86, 124.37, 123.96, 123.74, 123.69, 120.96, 120.92, 120.88, 120.36, 117.50, 73.70, 73.57, 21.18, 21.17, 19.05, 17.68.

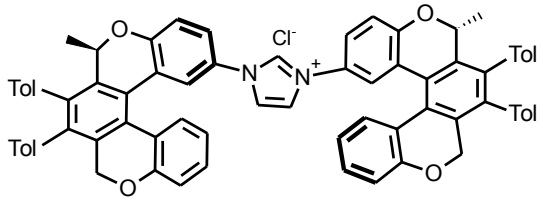


IR (KBr): 3140 w, 3050 w, 2982 m, 1618 vs, 1592 s, 1549 s, 1516 s, 1487 s, 1404 w, 1382 s, 1263 w, 1183 m, 1150 s, 1111 m, 1018 m, 981 w, 885 w, 837 m, 817 m cm^{-1}.

ESI MS: 1154 ($[M]^+$).

HR ESI MS: calcd for $C_{83}H_{65}O_4N_2$ 1153.4939, found 1153.4940.

(–)-(*M*,*M*)-1,3-Bis[(5*R*)-5-methyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[1,2-*c*:4,3-*c*′]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 162



Imidazolium chloride (–)-(*M*,*R*),(*M*,*R*)-**162** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M*,*R*)-**166** (47 mg, 0.095 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.4 µl, 0.047 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.047 mmol, 0.5 equiv.) in acetic acid (0.5 ml) at 45 °C for 37 min. The residue was flash

chromatographed on silica gel (dichloromethane–methanol 20:1 to 9:1) provided (–)-(*M,R*),(*M,R*)-**162** (31 mg, 62%) as pale white solid.

M.p.: 275.6-277.7°C (dichloromethane – methanol).

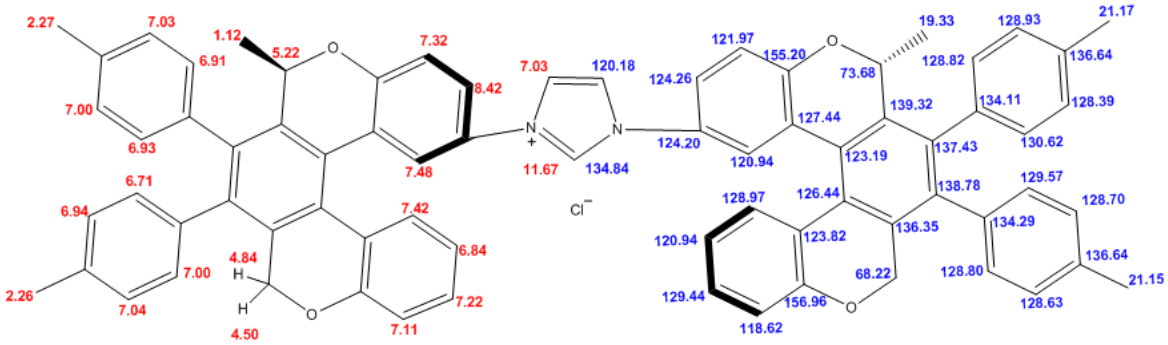
Optical rotation: $[\alpha]^{20}_{D}$ = -489° (c 0.255, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 214 (5.18), 270 (5.12), 335(4.61) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 424 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 11.67 (t, *J* = 1.6, 1H), 8.42 (dd, *J* = 8.8, 2.85, 2H), 7.48 (d, *J* = 2.85, 2H), 7.42 (dd, *J* = 7.9, 1.6, 2H), 7.32 (d, *J* = 8.8, 2H), 7.22 (ddd, *J* = 8.1, 7.3, 1.6, 2H), 7.11 (dd, *J* = 8.1, 1.3, 2H), 7.06 – 7.01 (m, 8H), 7.03 (d, *J* = 1.6, 2H), 7.01 – 6.98 (m, 2H), 6.95 – 6.89 (m, 6H), 6.74 – 6.69 (m, 2H), 5.22 (q, *J* = 6.7, 2H), 4.84 (d, *J* = 14.2, 2H), 4.50 (d, *J* = 14.2, 2H), 2.27 (s, 6H), 2.26 (s, 6H), 1.12 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 156.96, 155.20, 139.32, 138.78, 137.43, 136.64 (2C), 136.35, 134.84, 134.23, 134.11, 130.62, 129.57, 129.44, 128.97, 128.93, 128.82, 128.80, 128.70, 128.63, 128.39, 127.44, 126.44, 124.26, 124.20, 123.82, 123.19, 121.97, 120.94 (2C), 120.18, 118.62, 73.68, 68.22, 21.17, 21.15, 19.33.



IR ($CHCl_3$): 3141 w, 1602 m, 1583 m, 1546 s, 1518 s, 1492 s, sh, 1485 vs, 1451 s, 1445 s, sh, 1428 s, 1405 w, 1388 w, 1371 m, 1345 m, 1259 s, 1248 vs, 1184 m, 1127 m, 1094 w, 1065 s, 1036 s, 839 s, 819 m cm^{-1}.

ESI MS: 1025 ($[M]^+$).

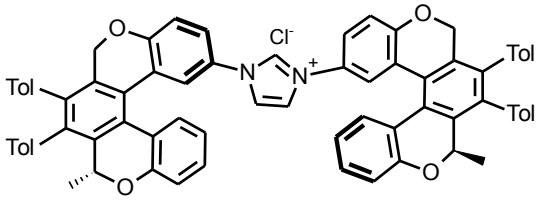
HR ESI MS: calcd for $C_{73}H_{57}O_4N_2$ 1025.4313, found 1025.4314.

IR ($CHCl_3$): 3061 vw, 3030 w, 1772 w, sh, 1764 s, 1620 m, 1590 w, sh, 1576 w, sh, 1556 w, 1496 m, 1429 w, 1370 m, 1198 s, sh, 1190 vs, 1088 m cm^{-1}.

EI MS: 346 ($M^{+\bullet}$, 25), 304 (100), 177 (12), 149 (15), 113 (12).

HR EI MS: calcd for $C_{12}H_8O_2{}^{35}ClI$ 345.9258, found 345.9261.

(–)-(*M*,*M*)-1,3-Bis[(2*R*)-2-methyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[1,2-*c*:4,3-*c′*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 163



Imidazolium chloride (–)-(*M,R*),(*M,R*)-**163** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M,R*)-**167** (39 mg, 0.079 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 4.5 µl, 0.039 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 3.0 µl, 0.039 mmol, 0.5 equiv.) in acetic acid (0.5 ml) at 45 °C for 42 min. The residue was flash chromatographed on silica gel (dichloromethane–methanol 20:1 to 9:1) provided (–)-(*M,R*),(*M,R*)-**163** (23 mg, 55%) as pale white solid.

M.p.: 290.5-295.3 °C (dichloromethane – methanol).

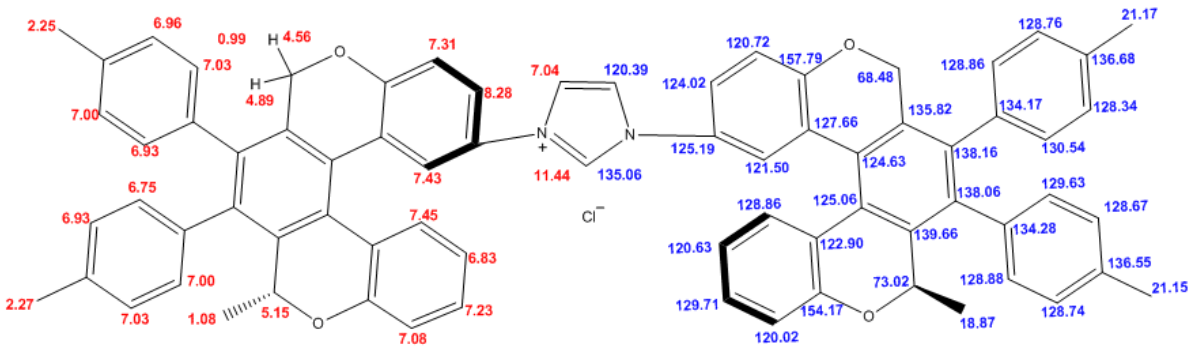
Optical rotation: $[\alpha]^{20}_D$ = -475° (c 0.194, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 212 (4.99), 270 (5.28), 334 (4.74) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 420 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 11.44 (bs, 1H), 8.28 (bd, *J* = 8.6, 2H), 7.45 (dd, *J* = 7.8, 1.6, 2H), 7.43 (d, *J* = 2.4, 2H), 7.31 (d, *J* = 8.6, 2H), 7.23 (ddd, *J* = 8.1, 7.3, 1.6, 2H), 7.08 (dd, *J* = 8.1, 1.2, 2H), 7.05 – 7.01 (m, 6H), 7.01 – 6.97 (m, 4H), 6.96 – 6.94 (m, 2H), 6.94 – 6.91 (m, 4H), 6.83 (ddd, *J* = 7.8, 7.3, 1,2, 2H), 6.76– 6.72 (m, 2H), 5.15 (q, *J* = 6.7, 2H), 4.89 (d, *J* = 14.3, 2H), 4.56 (d, *J* = 14.3, 2H), 2.27 (s, 6H), 2.25 (s, 6H), 1.08 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 157.79, 154.17, 139.66, 138.16, 138.06, 136.68, 136.55, 135.82, 135.06, 134.28, 134.17, 130.54, 129.71, 129.63, 128.88, 128.86 (2C), 128.76, 128.74, 128.67, 128.34, 127.66, 125.19, 125.06, 124.63, 124.02, 122.90, 121.50, 120.72, 120.63, 120.39, 120.02, 73.02, 68.48, 21.17, 21.15, 18.87.

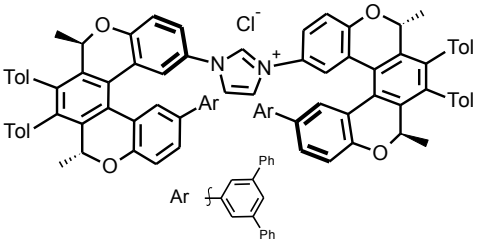


IR ($CHCl_3$): 3140 w, 3026 m, 2947 s, sh, 2929 s, 2852 w, sh, 1613 w, sh, 1603 m, 1570 vw, sh, 1546 s, 1518 s, 1485 s, 1462 m, sh, 1452 s, 1445 s, 1428 s, 1405 w, sh, 1374 w, sh, 1369 s, 1344 m, 1278 s, 1256 vs, 1243 s, 1235 s, 1184 m, 1067 vs, 1023 vs, 1012 s, 981 w, 820 m cm^{-1}.

ESI MS: 1025 ($[M]^+$).

HR ESI MS: calcd for $C_{73}H_{57}O_4N_2$ 1025.4313, found 1025.4314.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-(1,1':3',1''-terphenyl-5'-yl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 180a



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**180a** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M,R,R*)-**179a** (72 mg, 0.098 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 6.0 µl, 0.052 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 6.0 µl, 0.081 mmol, 0.8 equiv.) in acetic acid (0.5 ml) at 50 °C for 1.7 h. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**180a** (43 mg, 57%) as a pale white solid.

M.p.: 278-284 °C (dichloromethane – methanol).

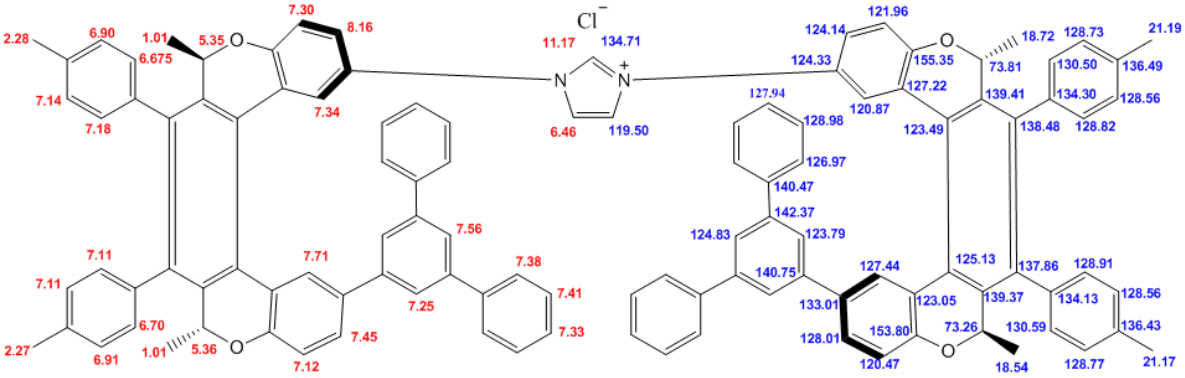
Optical rotation: $[\alpha]^{20}_D$ = -716° (c 0.313, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 265 (5.17), 342 (4.30) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 417 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 11.17 (bs, 1H), 8.16 (bdd, *J* = 8.8, 2.5, 2H), 7.71 (d, *J* = 2.3, 2H), 7.56 (t, *J* = 1.7, 2H), 7.45 (dd, *J* = 8.3, 2.3, 2H), 7.43 – 7.38 (m, 16H), 7.35 – 7.32 (m, 6H), 7.30 (d, *J* = 8.8, 2H), 7.25 (d, *J* = 1.7, 4H), 7.18 (m, 2H), 7.14 – 7.11 (m, 6H), 7.12 (d, *J* = 8.3, 2H), 6.91 – 6.89 (m, 4H), 6.70 (m, 2H), 6.675 (m, 2H), 6.46 (d, *J* = 1.5, 2H), 5.36 (q, *J* = 6.7, 2H), 5.35 (q, *J* = 6.7, 2H), 2.28 (s, 6H), 2.27 (s, 6H), 1.01 (d, *J* = 6.7, 12H).

^{13}C NMR (151 MHz, $CDCl_3$): 155.35, 153.80, 142.37, 140.75, 140.47, 139.41, 139.37, 138.48, 137.86, 136.49, 136.43, 134.71, 134.30, 134.13, 133.01, 130.59, 130.50, 128.98, 128.91, 128.82, 128.77, 128.73, 128.56 (2C), 128.01, 127.94, 127.44, 127.22, 126.97, 125.13, 124.83, 124.33, 124.14, 123.79, 123.49, 123.05, 121.96, 120.87, 120.47, 119.50, 73.81, 73.26, 21.19, 21.17, 18.72, 18.54.

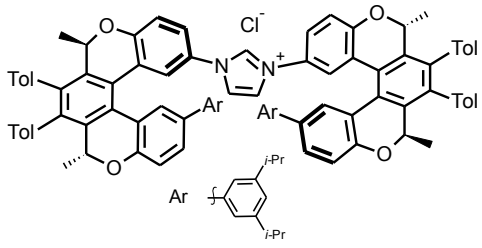


IR ($CHCl_3$): 3060 w, sh, 1595 s, 1547 m, 1518 s, 1497 s, 1489 s, 1441 m, 1426 m, 1414 m, 1405 w, sh, 1274 m, 1261 m, sh, 1250 m, 1184 w, 1148 m, 1109 m, 1085 m, 1073 w, sh, 1030 w, 1021 m, 957 w, sh, 881 m, 879 m, 839 m, 823 m, 719 m, 614 w, 534 w cm^{-1}.

ESI MS: 1509 ($[M]^+$).

HR ESI MS: calcd for $C_{111}H_{85}O_4N_2$ 1509.6504, found 1509.6509.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-12-[3,5-bis(1-methylethyl)phenyl]-2,5-dimethyl-3,4-bis(4-methyl-phenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c*′]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 180b



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**180b** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M,R,R*)-**179b** (77 mg, 0.115 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 7.0 µl, 0.061 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 5.0 µl, 0.067 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 45 °C for 40 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**180b** (52 mg, 64%) as pale white solid.

M.p.: 256-262 °C (dichloromethane – methanol).

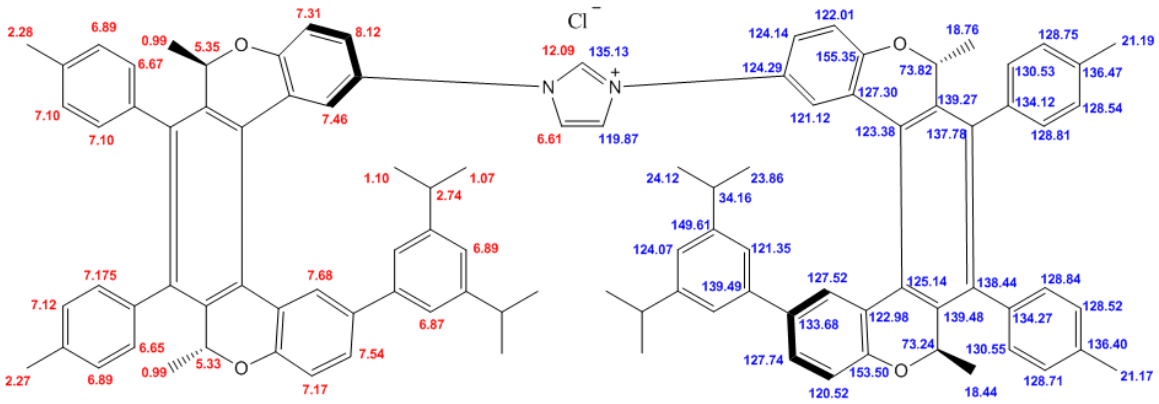
Optical rotation: $[\alpha]^{20}_D$ = -806° (c 0.275, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 264 (4.99), 342 (4.29) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 420 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 12.09 (s, 1H), 8.12 (bdd, *J* = 8.7, 2.7, 2H), 7.68 (d, *J* = 2.3, 2H), 7.54 (dd, *J* = 8.3, 2.3, 2H), 7.46 (d, *J* = 2.7, 2H), 7.31 (d, *J* = 8.7, 2H), 7.175 (m, 2H), 7.17 (d, *J* = 8.3, 2H), 7.12 (m, 2H), 7.10 (m, 4H), 6.90 – 6.88 (m, 6H), 6.87 (d, *J* = 1.7, 4H), 6.67 (m, 2H), 6.65 (m, 2H), 6.61 (d, *J* = 1.3, 2H), 5.35 (q, *J* = 6.7, 2H), 5.33 (q, *J* = 6.7, 2H), 2.74 (sept, *J* = 6.9, 4H), 2.28 (s, 6H), 2.27 (s, 6H), 1.10 (d, *J* = 6.7, 12H), 1.07 (d, *J* = 6.7, 12H), 0.99 (d, *J* = 6.7, 12H).

^{13}C NMR (151 MHz, $CDCl_3$): 155.35, 153.50, 149.61, 139.49, 139.48, 139.27, 138.44, 137.78, 136.47, 136.40, 135.13, 134.27, 134.12, 133.68, 130.55, 130.53, 128.84, 128.81, 128.75, 128.71, 128.54, 128.52, 127.74, 127.52, 127,30, 125.14, 124.29, 124.14, 124.07, 123.38, 122.98, 122.01, 121.35, 121.12, 120.52, 119.87, 73.82, 73.24, 34.16, 24.12, 23.86, 21.19, 21.17, 18.76, 18.44.

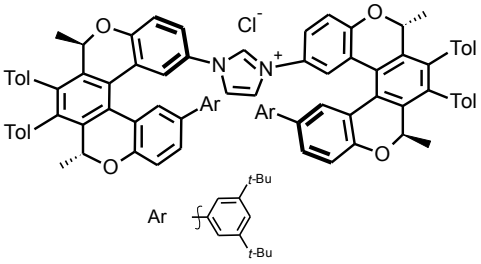


IR ($CHCl_3$): 3049 w, sh, 2962 m, 2928 w, 1598 w, 1545 w, 1518 w, 1457 w, sh, 1428 w, 1384 w, 1369 vw, 1343 w, sh, 1260 w, 1148 w, 1132 w, 1108 w, 1090 w, 1067 m, 876 w, 839 w, 823 w, 569 w, 525 w, 467 w cm^{-1}.

ESI MS: 1374 ($[M]^+$).

HR ESI MS: calcd for $C_{99}H_{93}O_4N_2$ 1373.7130, found 1373.7130.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-12-(3,5-di-*tert*-butylphenyl)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c*′]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 180c



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**180c** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M,R,R*)-**179c** (50 mg, 0.072 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.6 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.8 equiv.) in acetic acid (0.5 ml) at 45 °C for 50 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**180c** (43 mg, 82%) as a pale white solid.

M.p.: 256-259 °C (dichloromethane – methanol).

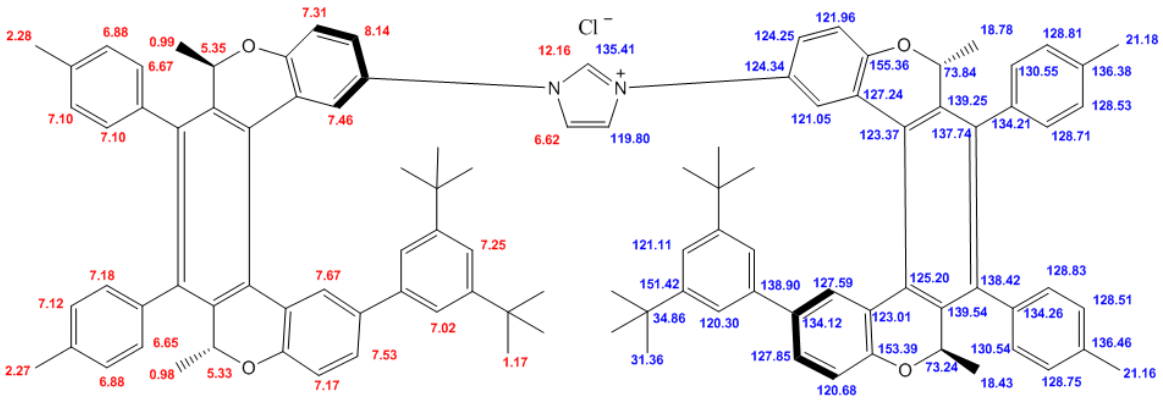
Optical rotation: $[\alpha]^{20}_D$ = -808° (c 0.258, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 263 (5.02), 343 (4.33) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 419 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 12.16 (s, 1H), 8.14 (dd, *J* = 8.7, 2.6, 2H), 7.67 (d, *J* = 2.3, 2H), 7.53 (dd, *J* = 8.3, 2.3, 2H), 7.46 (d, *J* = 2.6, 2H), 7.31 (d, *J* = 8.7, 2H), 7.25 (t, *J* = 1.8, 2H), 7.18 (m, 2H), 7.17 (d, *J* = 8.3, 2H), 7.12 (m, 2H), 7.10 (m, 4H), 7.02 (d, *J* = 1.8, 4H), 6.89 – 6.86 (m, 4H), 6.67 (m, 2H), 6.65 (m, 2H), 6.62 (d, *J* = 0.9, 2H), 5.35 (q, *J* = 6.7, 2H), 5.33 (q, *J* = 6.7, 2H), 2.28 (s, 6H), 2.27 (s, 6H), 1.17 (s, 36H), 0.99 (d, *J* = 6.7, 6H), 0.98 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 155.36, 153.39, 151.42, 139.54, 139.25, 138.90, 138.42, 137.74, 136.46, 136.38, 135.41, 134.26, 134.21, 134.12, 130.55, 130.54, 128.83, 128.81, 128.75, 128.71, 128.53, 128.51, 127.85, 127.59, 127.24, 125.20, 124.34, 124.25, 123.37, 123.01, 121.96, 121.11, 121.05, 120.68, 120.30, 119.80, 73.84, 73.24, 34.86, 31.36, 21.18, 21.16, 18.78, 18.43.

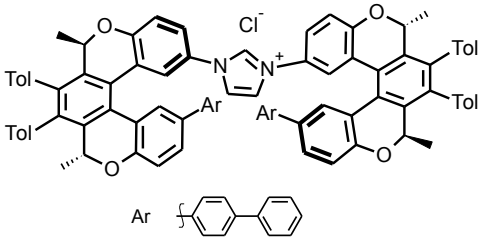


IR ($CHCl_3$): 3052 w, sh, 2966 vs, 2871 w, 1545 w, 1518 m, 1445 w, 1425 m, 1405 w, sh, 1395 w, 1368 m, 1343 w, 1330 w, sh, 1260 m, 1184 w, 1131 w, 1091 w, 1067 s, 1058 m, 838 m, 824 m, 808 m, 715 vw cm^{-1}.

ESI MS: 1430 ($[M]^+$).

HR ESI MS: calcd for $C_{103}H_{101}O_4N_2$ 1429.7756, found 1429.7755.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-12-biphenyl-4-yl-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydro-benzo[1,2-*c*:4,3-*c′*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 180d



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**180d** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M,R,R*)-**179d** (57 mg, 0.086 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 45 °C for 85 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**180d** (50 mg, 83%) as a pale white solid.

M.p.: 294-295 °C (dichloromethane – methanol).

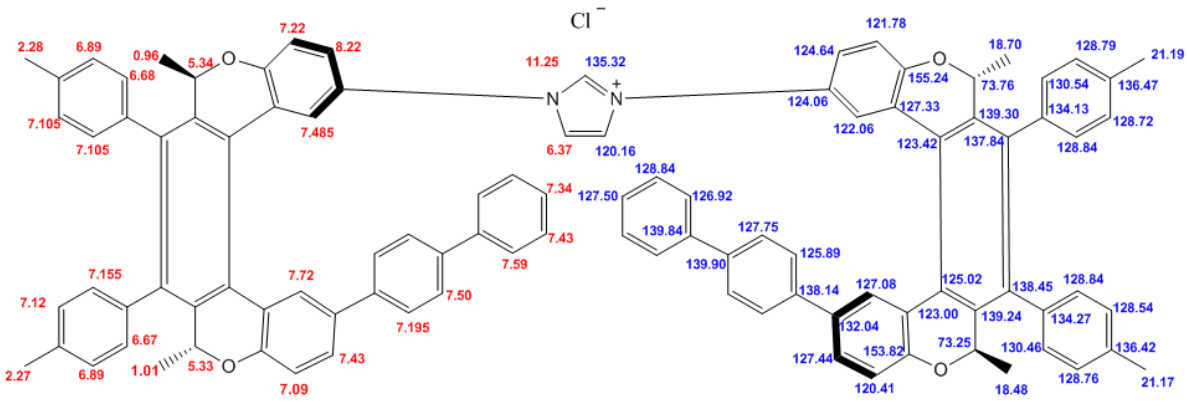
Optical rotation: $[\alpha]^{20}_D$ = -825° (c 0.273, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 274 (5.13), 300 (4.89), 350 (4.33) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 423 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 11.25 (s, 1H), 8.22 (dd, *J* = 8.8, 2.6, 2H), 7.72 (d, *J* = 2.3, 2H), 7.59 (m, 4H), 7.50 (m, 4H), 7.485 (d, *J* = 2.6, 2H), 7.44 – 7.42 (m, 6H), 7.34 (tt, *J* = 7.4, 1.2, 2H), 7.22 (d, *J* = 8.8, 2H), 7.195 (m, 4H), 7.155 (m, 2H), 7.12 (m, 2H), 7.105 (m, 4H), 7.09 (d, *J* = 8.3, 2H), 6.89 (m, 4H), 6.68 (m, 2H), 6.67 (m, 2H), 6.37 (d, *J* = 1.6, 2H), 5.34 (q, *J* = 6.7, 2H), 5.33 (q, *J* = 6.7, 2H), 2.28 (s, 6H), 2.27 (s, 6H), 1.01 (d, *J* = 6.7, 6H), 0.96 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 155.24, 153.82, 139.90, 139.84, 139.30, 139.24, 138.45, 138.14, 137.84, 136.47, 136.42, 135.32, 134.27, 134.13, 132.04, 130.54, 130.46, 128.84 (3C), 128.79, 128.76, 128.72, 128.54, 127.75, 127.50, 127.44, 127.33, 127.08, 126.92, 125.89, 125.02, 124.64, 124.06, 123.42, 123.00, 122.06, 121.78, 120.41, 120.16, 73.76, 73.25, 21.19, 21.17, 18.70, 18.48.

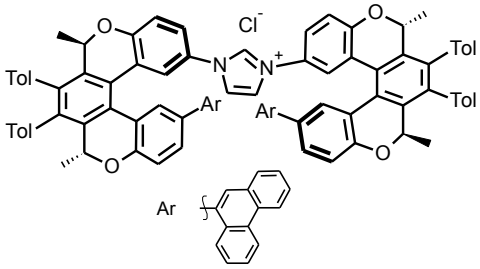


IR ($CHCl_3$): 3052 w, sh, 1602 w, 1585 vw, 1544 w, 1518 m, 1482 s, 1448 w, sh, 1435 m, 1401 w, 1369 m, 1341 vw, 1330 vw, 1132 w, 1109 w, 1090 w, 1065 w, 1006 w, 943 vw, 838 m, 699 m, 508 w cm^{-1}.

ESI MS: 1358 ($[M]^+$).

HR ESI MS: calcd for $C_{99}H_{77}O_4N_2$ 1357.5878, found 1357.5886.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-phenanthren-9-yl-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 180e



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**180e** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M,R,R*)-**179e** (58 mg, 0.085 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 50 °C for 80 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**180e** (50 mg, 82%) as a pale white solid.

M.p.: 313-319 °C (dichloromethane – methanol).

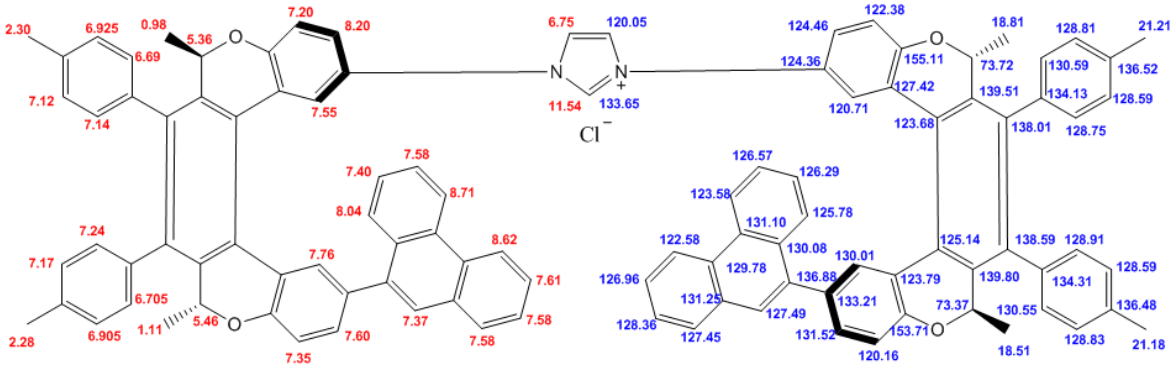
Optical rotation: $[\alpha]^{20}_D$ = -799° (c 0.301, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 259 (5.11), 300 (4.65), 338 (4.35) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 421 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 11.54 (s, 1H), 8.71 (d, J = 8.3, 2H), 8.62 (d, J = 8.3, 2H), 8.20 (bs, 2H), 8.04 (d, J = 7.8, 2H), 7.76 (d, J = 1.9, 2H), 7.61 – 7.55 (m, 12H), 7.35 (d, J = 8.0, 2H), 7.40 (t, J = 7.8, 2H), 7.37 (bs, 2H), 7.24 (m, 2H), 7.20 (bs, 2H), 7.17 (m, 2H), 7.14 (m, 2H), 7.12 (m, 2H), 6.925 (m, 2H), 6.905 (m, 2H), 6.75 (bs, 2H), 6.705 (m, 2H), 6.69 (m, 2H), 5.46 (q, J = 6.7, 2H), 5.36 (bq, J = 6.7, 2H), 2.30 (s, 6H), 2.28 (s, 6H), 1.11 (d, J = 6.7, 6H), 0.98 (bd, J = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 155.11, 153.71, 139.80, 139.51, 138.59, 138.01, 136.88, 136.52, 136.48, 134.31, 134.13, 133.65, 133.21, 131.52, 131.25, 131.10, 130.59, 130.55, 130.08, 130.01, 129.78, 128.91, 128.83, 128.81, 128.75, 128.59 (2C), 128.36, 127.49, 127.45, 127.42, 126.96, 126.57, 126.29, 125.78, 125.14, 124.46, 124.36, 123.79, 123.68, 123.58, 122.58, 122.38, 120.71, 120.16, 120.05, 73.72, 73.37, 21.21, 21.18, 18.81, 18.51.

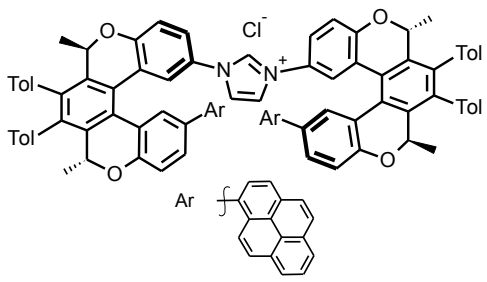


IR ($CHCl_3$): 3083 w, 3046 w, 1603 w, 1543 m, 1526 vw, 1517 s, 1451 w, 1432 m, 1402 w, 1344 w, 1308 vw, 1261 m, 1243 m, sh, 1184 w, 1169 w, sh, 1150 s, 1129 m, 1089 m, 1088 m, 1066 s, 1037 w, sh, 947 vw, 868 m, 839 m, 830 m, 808 m, 501 w cm^{-1}.

ESI MS: 1406 ($[M]^+$).

HR ESI MS: calcd for $C_{103}H_{77}O_4N_2$ 1405.5878, found 1405.5876.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-pyren-1-yl-2,5-dihydro-benzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 180f



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**180f** was synthesised according to the *General procedure D* from oxa[5]helicene amine (–)-(*M,R,R*)-**179f** (63 mg, 0.089 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 55 °C for 3.7 h. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**180f** (40 mg, 61%) as a pale white solid.

M.p.: 319-325 °C (dichloromethane – methanol).

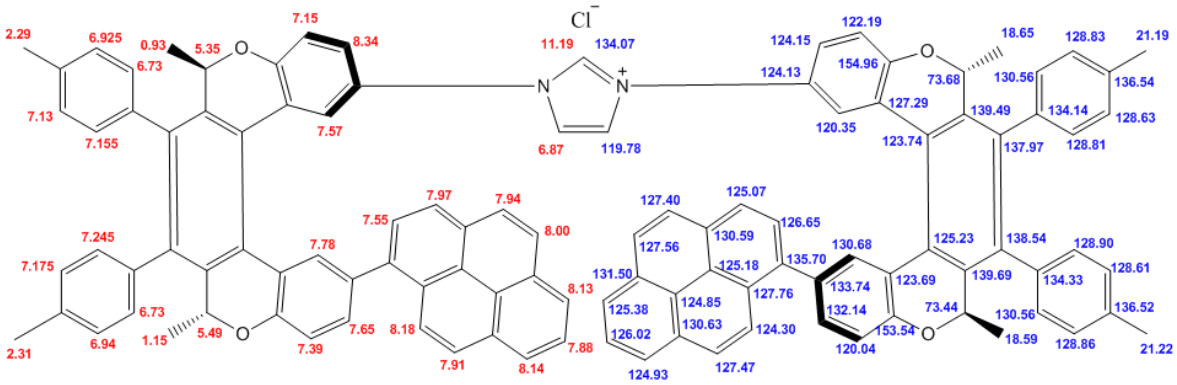
Optical rotation: $[\alpha]^{20}_D$ = -952° (c 0.353, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 237 (5.11), 270 (5.09), 278 (5.08), 346 (4.88) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 350 nm): λ_{max} = 437 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 11.19 (s, 1H), 8.34 (bd, *J* = 7.6, 2H), 8.18 (d, *J* = 9.2, 2H), 8.14 (dd, *J* = 7.6, 1.1, 2H), 8.13 (dd, *J* = 7.6, 1.1, 2H), 8.00 (d, *J* = 9.0, 2H), 7.97 (d, *J* = 7.9, 2H), 7.94 (d, *J* = 9.0, 2H), 7.91 (d, *J* = 9.2, 2H), 7.88 (t, *J* = 7.6, 2H), 7.78 (d, *J* = 2.2, 2H), 7.65 (dd, *J* = 8.2, 2.2, 2H), 7.57 (bs, 2H), 7.55 (d, *J* = 7.9, 2H), 7.39 (d, *J* = 8.2, 2H), 7.245 (m, 2H), 7.175 (m, 2H), 7.155 (m, 2H), 7.15 (bs, 2H), 7.13 (m, 2H), 6.94 (m, 2H), 6.925 (m, 2H), 6.87 (bs, 2H), 6.73 (m, 4H), 5.49 (q, *J* = 6.7, 2H), 5.35 (q, *J* = 6.7, 2H), 2.31 (s, 6H), 2.29 (s, 6H), 1.15 (d, *J* = 6.7, 6H), 0.93 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 154.96, 153.54, 139.69, 139.49, 138.54, 137.97, 136.54, 136.52, 135.70, 134.33, 134.14, 134.07, 133.74, 132.14, 131.50, 130.68, 130.63, 130.59, 130.56 (2C), 128.90, 128.86, 128.83, 128.81, 128.63, 128.61, 127.76, 127.56, 127.47, 127.40, 127.29, 126.65, 126.02, 125.38, 125.23, 125.18, 125.07, 124.93, 124.85, 124.30, 124.15, 124.13, 123.74, 123.69, 122.19, 120.35, 120.04, 119.78, 73.68, 73.44, 21.22, 21.19, 18.65, 18.59.

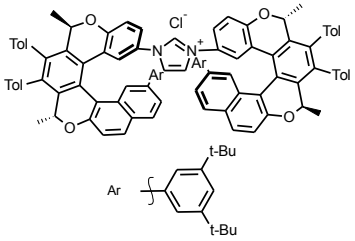


IR ($CHCl_3$): 3049 w, sh, 1586 vw, 1545 w, 1517 m, 1445 w, 1431 m, 1416 vw, 1405 w, 1360 m, 1343 w, 1261 m, 1184 m, 1133 w, 1066 m, 840 m, 825 m, 817 w, 808 vw, 709 vw cm^{-1}.

ESI MS: 1454 ($[M]^+$).

HR ESI MS: calcd for $C_{107}H_{77}O_4N_2$ 1453.5878, found 1453.5884.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-11-(3,5-di-*tert*-butylphenyl)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[*f*]benzo-[1,2-*c*:4,3-*c'*]dichromen-14-yl]-1*H*-imidazol-3-ium chloride 208



Imidazolium chloride (–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**208** was synthesised according to the *General procedure D* from oxa[6]helicene amine (–)-(*M*,*R*,*R*)-**194** (49.5 mg, 0.0662 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 4.0 µl, 0.035 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 3.3 µl, 0.044 mmol, 0.7 equiv.) in acetic acid (0.5 ml) at 55 °C for 35 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 30:1) provided (–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**208** (35 mg, 69%) as a pale orange solid.

M.p.: 273.9-275.1 °C (dichloromethane – methanol).

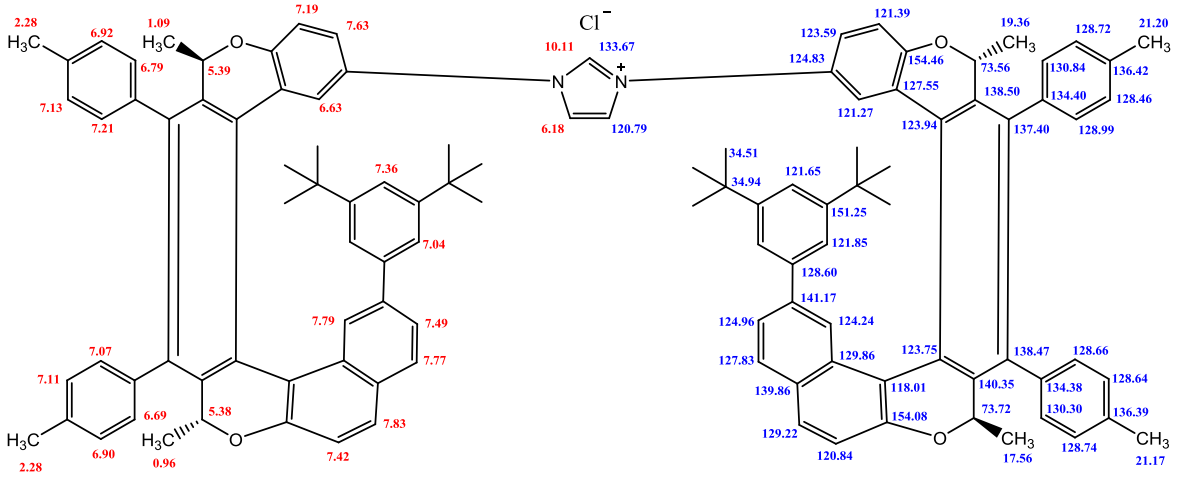
Optical rotation: $[\alpha]^{20}_D$ = -771° (c 0.183, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 265 (5.14), 317 (4.61) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 380 nm): λ_{max} = 436 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 10.11 (bs, 1H), 7.83 (dd, *J* = 8.6, 0.7, 2H), 7.79 (dt, *J* = 1.8, 0.7, 2H), 7.77 (bd, *J* = 8.4, 0.7, 2H), 7.63 (dd, *J* = 8.7, 2.8, 2H), 7.49 (dd, *J* = 8.4, 1.8, 2H), 7.42 (d, *J* = 8.6, 2H), 7.36 (t, *J* = 1.8, 2H), 7.21 (m, 2H), 7.19 (d, *J* = 8.7, 2H), 7.13 (m, 2H), 7.11 (m, 2H), 7.07 (m, 2H), 7.04 (d, *J* = 1.8, 4H), 6.92 (m, 2H), 6.90 (m, 2H), 6.79 (m, 2H), 6.69 (m, 2H), 6.63 (d, *J* = 2.8, 2H), 6.18 (d, *J* = 1.7, 2H), 5.39 (q, *J* = 6.7, 2H), 5.38 (q, *J* = 6.7, 2H), 2.28 (bs, 12H), 1.35 (s, 36H), 1.09 (d, *J* = 6.7, 6H), 0.96 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 154.46, 154.08, 151.25, 141.17, 140.35, 139.86, 138.50, 138.47, 137.40, 136.42, 136.39, 134.40, 134.38, 133.67, 130.84, 130.30, 129.86, 129.22, 128.99, 128.74, 128.72, 128.66, 128.64, 128.60, 128.46, 127.83, 127.55, 124.96, 124.83, 124.24, 123.94, 123.75, 123.59, 121.85, 121.65, 121.39, 121.27, 120.84, 120.79, 118.01, 73.72, 73.56, 34.94, 31.51, 21.20, 21.17, 19.36, 17.56.

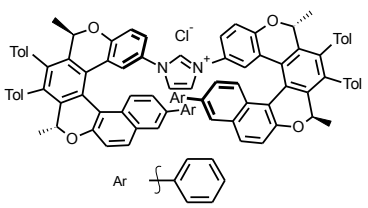


IR ($CHCl_3$): 3135 vw, 2988 w, 2966 w, 2933 w, 2867 w, 1618 w, 1604 w, sh, 1588 w, 1546 vw, 1517 w, 1442 w, 1429 vw, 1393 vw, 1380 w, 1370 w, 1365 vw, 1183 w, 1151 vw, 1055 m, 1021 w, 848 s, 691 s cm^{-1}.

ESI MS: 1530 ($[M]^+$).

HR ESI MS: calcd for $C_{111}H_{105}O_4N_2$ 1529.8069, found 1529.8064.

(–)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-10-phenyl-2,5-dihydrobenzo-[*f*]benzo-[1,2-*c*:4,3-*c′*]dichromen-14-yl]-1*H*-imidazol-3-ium chloride 207



Imidazolium chloride (–)-(*M,R,R*),(*M,R,R*)-**207** was synthesised according to the *General procedure D* from oxa[6]helicene amine (–)-(*M,R,R*)-**206** (47 mg, 0.074 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 4.0 µl, 0.035 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.7 equiv.) in acetic acid (0.5 ml) at 55 °C for 46 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (–)-(*M,R,R*),(*M,R,R*)-**207** (33 mg, 67%) as an off-white solid.

M.p.: 307.0-310.3 °C (dichloromethane – methanol).

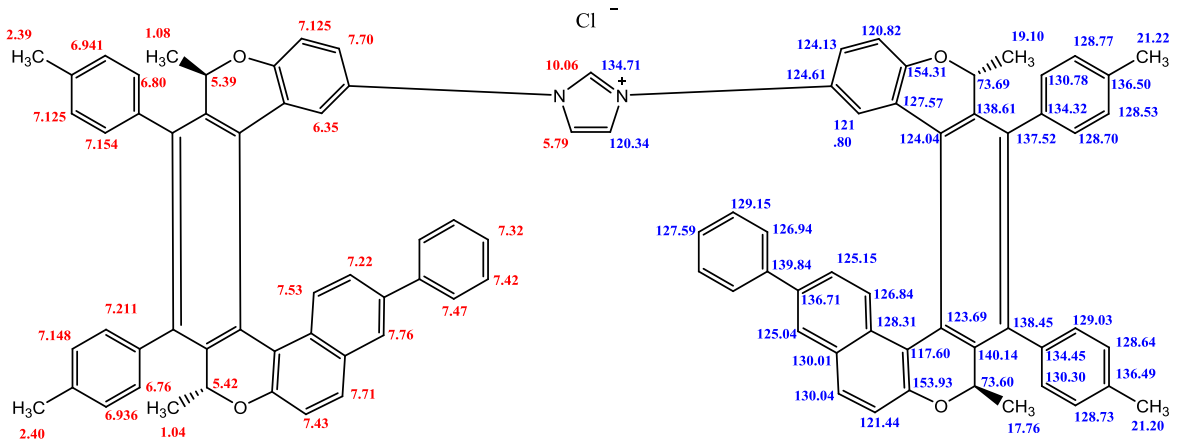
Optical rotation: $[\alpha]^{20}_D$ = -763° (c 0.206, $CHCl_3$).

UV/Vis (tetrahydrofuran): λ_{max} (log ε) = 273 (5.08), 375 (4.29) nm.

Fluorescence (tetrahydrofuran, λ_{exc} = 370 nm): λ_{max} = 430 nm.

^{1}H NMR (600 MHz, $CDCl_3$): 10.06 (bs, 1H), 7.76 (bd, *J* = 2.0, 2H), 7.71 (dd, *J* = 8.6, 0.7, 2H), 7.70 (dd, *J* = 8.6, 2.7, 2H), 7.53 (dt, *J* = 8.9, 0.7, 2H), 7.47 (m, 4H), 7.43 (d, *J* = 8.6, 2H), 7.42 (m, 4H), 7.32 (m, 2H), 7.22 (dd, *J* = 8.9, 2.0, 2H), 7.21 (m, 2H), 7.154 (m, 2H), 7.148 (m, 2H), 7.125 (d, *J* = 8.6, 2H), 7.125 (m, 2H), 6.94 (m, 4H), 6.80 (m, 2H), 6.76 (m, 2H), 6.35 (d, *J* = 2.7, 2H), 5.79 (d, *J* = 1.5, 2H), 5.42 (q, *J* = 6.7, 2H), 5.39 (q, *J* = 6.7, 2H), 2.40 (s, 6H), 2.39 (s, 6H), 1.08 (d, *J* = 6.7, 6H), 1.04 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): 154.31, 153.93, 140.14, 139.84, 138.61, 138.45, 137.52, 136.71, 136.50, 136.49, 134.71, 134.45, 134.32, 130.78, 130.30, 130.04, 130.01, 129.15, 129.03, 128.77, 128.73, 128.70, 128.64, 128.53, 128.31, 127.59, 127.57, 126.94, 126.84, 125.15, 125.04, 124.61, 124.13, 124.04, 123.69, 121.80, 121.44, 120.82, 120.34, 117.60, 73.69, 73.60, 21.22, 21.20, 19.10, 17.76.



IR ($CHCl_3$): 3137 w, 3049 w, sh, 1619 w, 1592 m, 1579 m, 1547 m, 1517 m, 1490 vs, 1451 m, sh, 1445 m, 1431 m, 1403 w, 1345 w, sh, 1308 w, sh, 1184 m, 1151 m, sh, 1125 w, 1099 m, 1077 m, 1026 m, 998 w, 839 m, 820 m, 690 w, sh, 558 w cm^{-1}.

ESI MS: 1306 ($[M]^+$).

HR ESI MS: calcd for $C_{95}H_{73}O_4N_2$ 1305.5565, found 1305.5561.

Ni^0-Catalysed enantioselective [2+2+2] cycloisomerisation of triynes 43 and 160

Drying of $Ni(acac)_2$:

The commercially available nickel(II) acetylacetonate was heated in a Schlenk flask under vacuum at 150 °C for 4 h, then it was allowed to cool down to room temperature and flushed with argon. This material was used for catalytic experiments for at least one month without any decrease in reactivity.

Preparation of EtMgCl stock solution:

The commercially available EtMgCl solution (5 ml, 2M in THF) was diluted with freshly distilled THF (20 ml) to form an approximately 0.4 M solution. The exact concentration was determined before each experiment by titration with iodine.

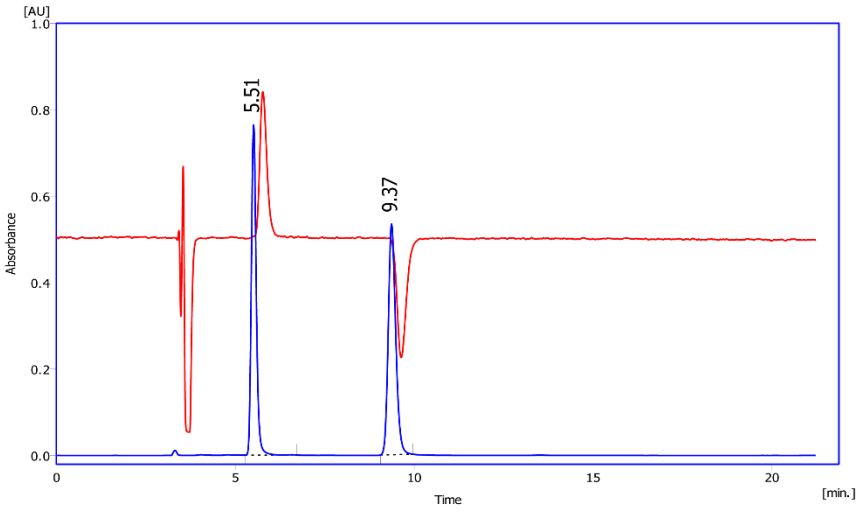
*Representative procedure for [2+2+2] cycloisomerisation of triyne **43** using chiral imidazolium chloride* (–)-(*M,R,R*),(*M,R,R*)-**136a** *as a ligand:*

A dry Schlenk flask was charged with $Ni(acac)_2$ (1.2 mg, 0.0047 mmol, 20 mol%) and imidazolium chloride **136a** (11 mg, 0.010 mmol, 44 mol%) and heated at 80 °C for 1 h under vacuum. After cooling down to room temperature and flushing with argon, the freshly distilled tetrahydrofuran (300 µl) was added followed by ethylmagnesium chloride (0.36 M in THF, 58 µl, 0.021 mmol, 92 mol%). The solution immediately turned black. After 2 min, triyne **43** (10 mg, 0.023 mmol, 1.0 equiv.) in tetrahydrofuran (200 µl) was injected and the reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated and the residue was filtered through a short pad of silica gel (hexane-dichloromethane 7:1) to get the crude enantioenriched [6]helicene (+)-(*P*)-**46** (7.2 mg). HPLC analysis (Chiralpak IA, heptane–chloroform 7:2) showed the conversion >90% and 41% *ee*.

HPLC analyses of dibenzo[6]helicene 46 and dibenzo[7]helicene 161

HPLC analyses were performed on a Chiralpak IA column (250 × 4.6 mm, 5 µm, Chiral Technologies) using an instrument consisting of an isocratic HPLC pump (Knauer Smartline 1000), a variable-wavelength UV detector set at 254 nm (Knauer Smartline 2500), a polarimetric detector (Chiralyser LED 426 nm, IBZ Messtechnik) and a PC workstation with Clarity software (Dataapex). Heptane-chloroform (70:30) was used as a mobile phase at a flow rate of 1.0 ml/min. For analyses, the samples were dissolved in HPLC grade chloroform (ca 1 mg/ml) and filtered through a 0.45 µm PTFE syringe filter before injection (ca 1 µl).

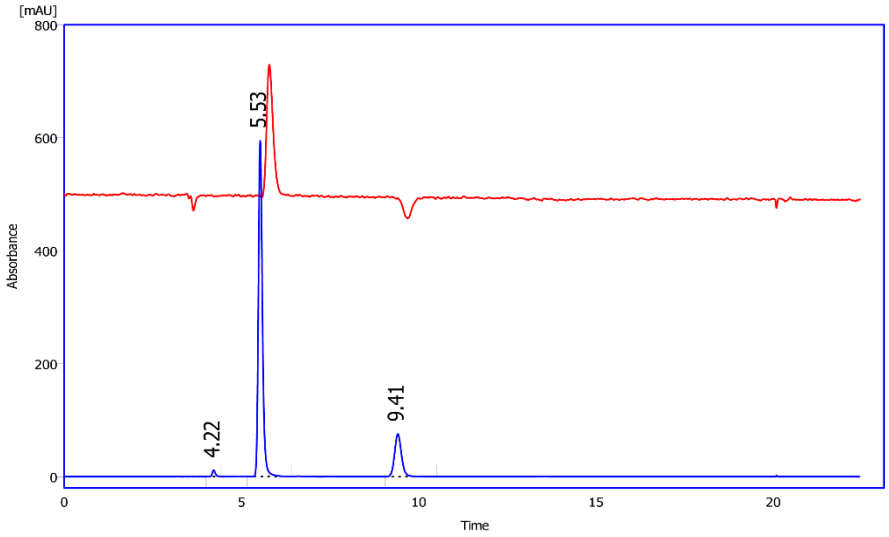
Conversions as well as enantiomeric excesses were determined by integration of the corresponding peaks of the UV-absorption (254 nm) traces in the respective HPLC chromatograms *via* the calibration curve. The authentic samples of the racemic [6]- and [7]helicenes, required for identification of peaks corresponding to the individual enantiomers, were prepared in our group earlier.



Result Table (Uncal - C:\Clarity_Samal\Data\SAM-[6]dibn_public2 - S 2500: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.510	7297.104	764.381	48.68	58.9	0.15	
2	9.367	7692.849	533.652	51.32	41.1	0.22	
	Total	14989.953	1298.033	100.00	100.0		

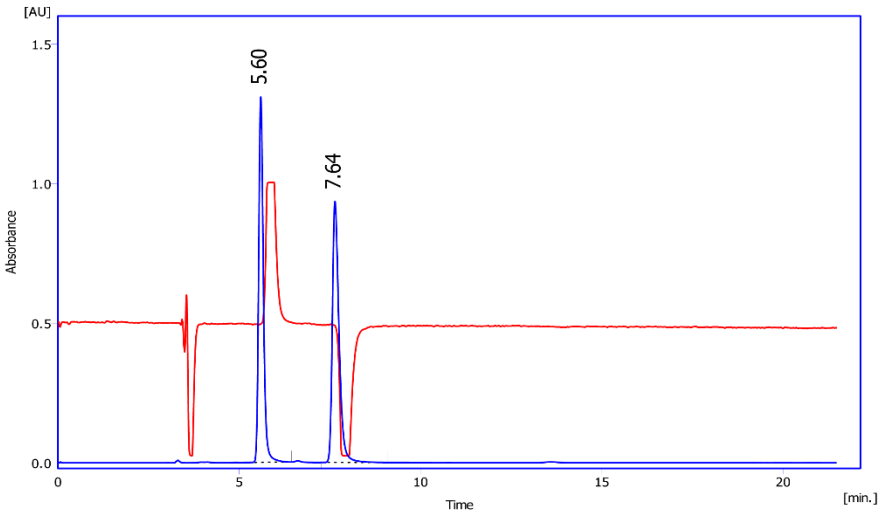
Figure S1: HPLC chromatogram (Chiralpak IA column, heptane – chloroform 7:3) of *rac*-[6]helicene **46** (blue: UV detector, red: downstream polarimetric detector).



Result Table (Uncal - C:\Clarity_Samal\Data\SAM-[6]dibn_public_cat1 - S 2500: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.217	68.633	11.354	1.19	1.7	0.09	
2	5.527	4671.710	594.269	81.00	87.2	0.12	
3	9.410	1027.138	75.549	17.81	11.1	0.21	
	Total	5767.481	681.172	100.00	100.0		

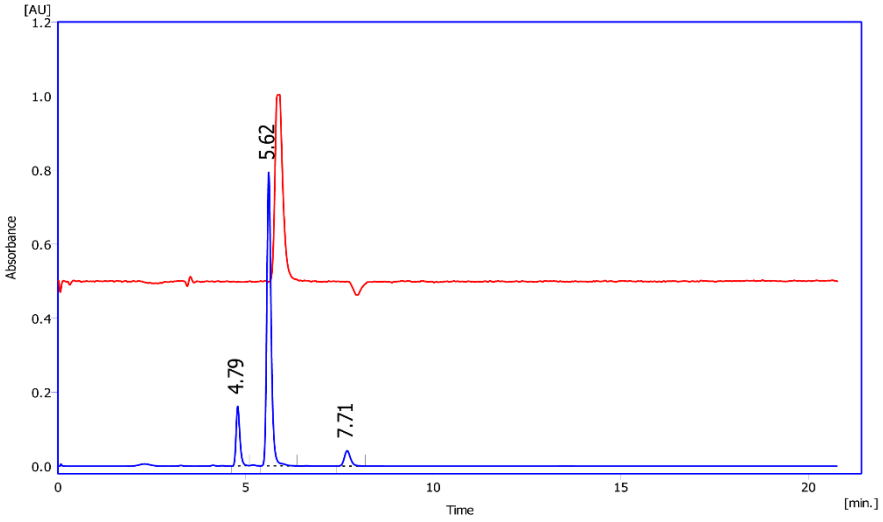
Figure S2: HPLC chromatogram (Chiralpak IA column, heptane – chloroform 7:3) of (*P*)-[6]helicene **46** (64% *ee*) after cyclisation, where (–)-(*M,R,R*),(*M,R,R*)-**136a** was used as the chiral ligand. The peak at 4.22 min. corresponds to the starting material (blue: UV detector, red: downstream polarimetric detector).



Result Table (Uncal - C:\Clarity_Samal\Data\SAM-[7]dibn_public2 - S 2500: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.597	11801.091	1308.922	49.73	58.3	0.14	
2	7.640	11928.425	934.606	50.27	41.7	0.19	
	Total	23729.516	2243.528	100.00	100.0		

Figure S3: HPLC chromatogram (Chiralpak IA column, heptane – chloroform 7:3) of *rac*-[7]helicene **161** (blue: UV detector, red: downstream polarimetric detector).



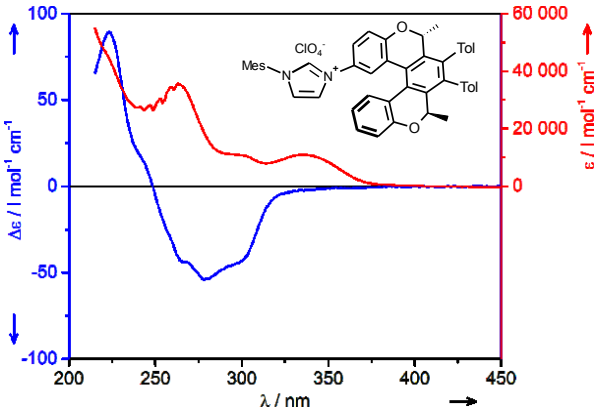
Result Table (Uncal - C:\Clarity_Samal\Data\SAM-[7]dibn_public_cat2 - S 2500: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.790	1125.959	160.856	14.11	16.2	0.11	
2	5.617	6379.459	793.017	79.95	79.7	0.12	
3	7.707	474.256	41.312	5.94	4.2	0.18	
	Total	7979.674	995.184	100.00	100.0		

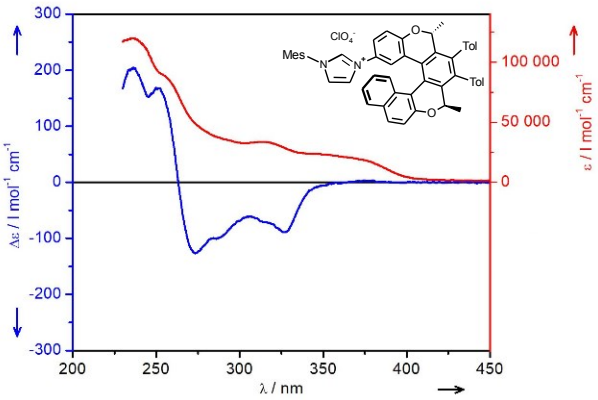
Figure S4: HPLC chromatogram (Chiralpak IA column, heptane – chloroform 7:3) of (*P*)-[7]helicene **161** (86% *ee*) after cyclisation, where (–)-(*M,R,R*),(*M,R,R*)-**180b** was used as the chiral ligand. The peak at 4.79 min. corresponds to the starting material (blue: UV detector, red: downstream polarimetric detector).

The experimental UV and CD spectra of compounds (–)-(*M*,*R*,*R*)-**134**, (–)-(*M*,*R*,*R*)-**135**, (–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**136a,** (–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**137a**, (–)-(*M*,*R*,*R*)-**138a**, (–)-(*M*,*R*,*R*)-**139a**, (–)-(*M*,*R*),(*M*,*R*)-**162**, (–)-(*M*,*R*),(*M*,*R*)-**163**, (–)-(*M*,*R*)-**166**, (–)-(*M*,*R*)-**167**, (–)-(*M*,*R*,*R*)-**179a-f**, (–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**180a-f,** (–)-(*M*,*R*,*R*)-**194**, (–)-(*M*,*R*,*R*)-**206**, (–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**207** and (–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**208**.

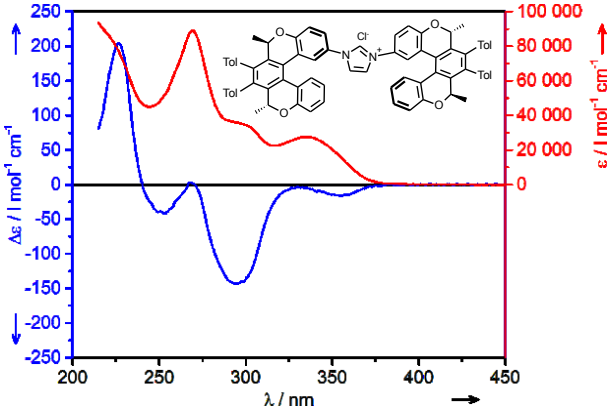
(–)-(*M*,*R*,*R*)-**138a**



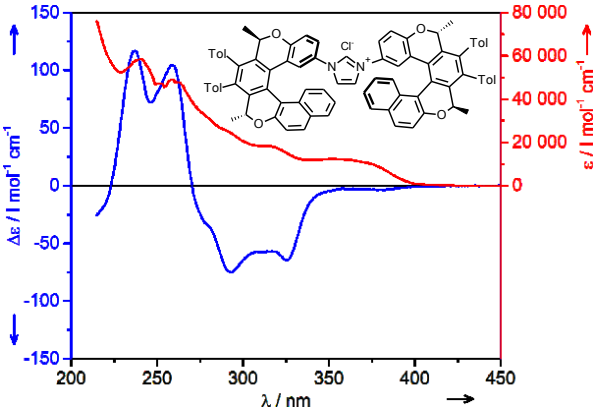
(–)-(*M*,*R*,*R*)-**139a**



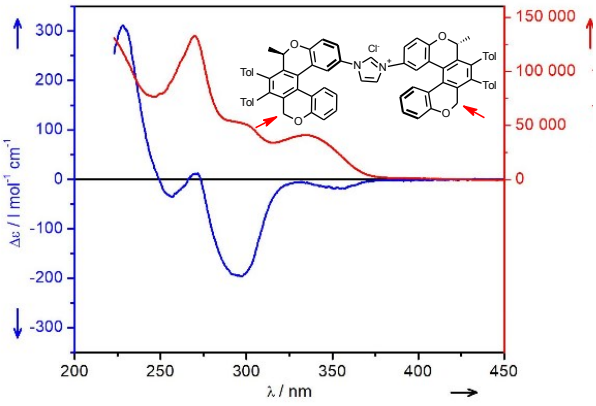
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**136a**



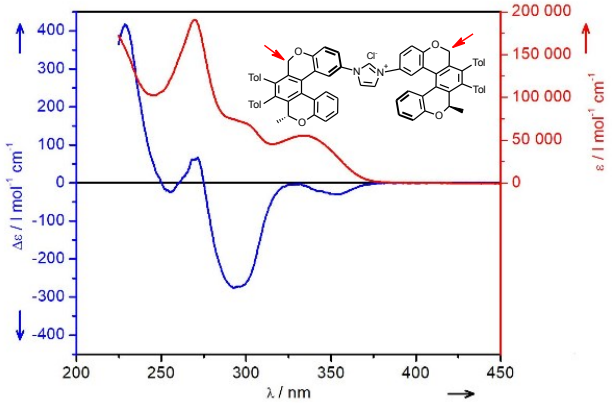
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**137a**



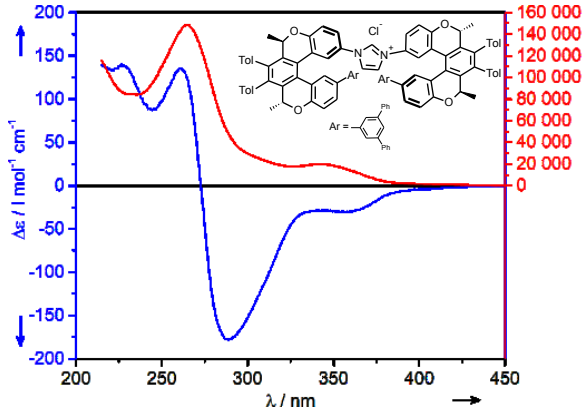
(–)-(*M*,*R*),(*M*,*R*)-**162**



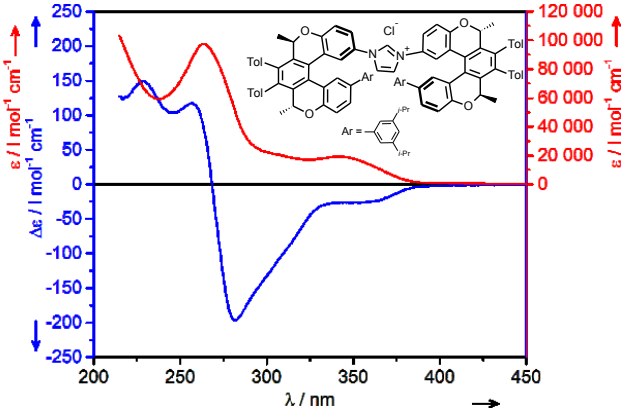
(–)-(*M*,*R*),(*M*,*R*)-**163**



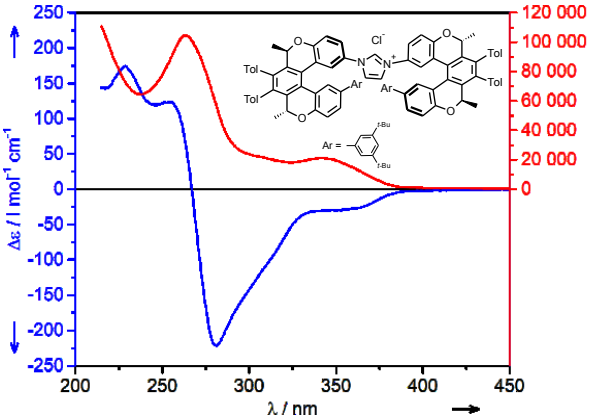
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**180a**



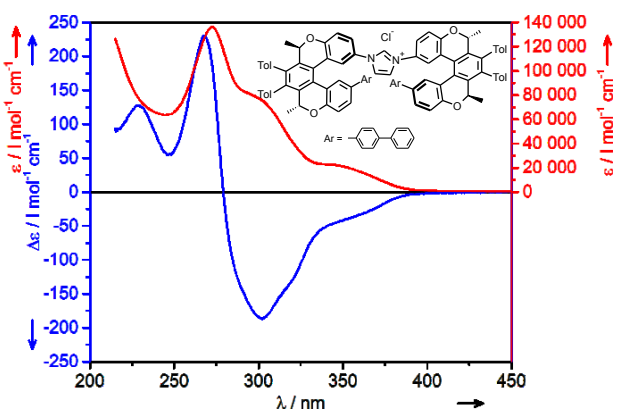
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**180b**



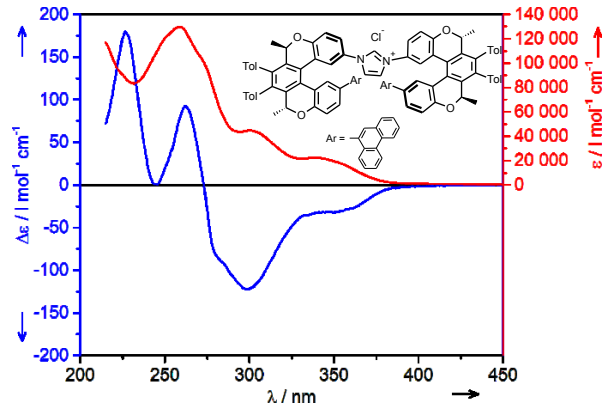
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**180c**



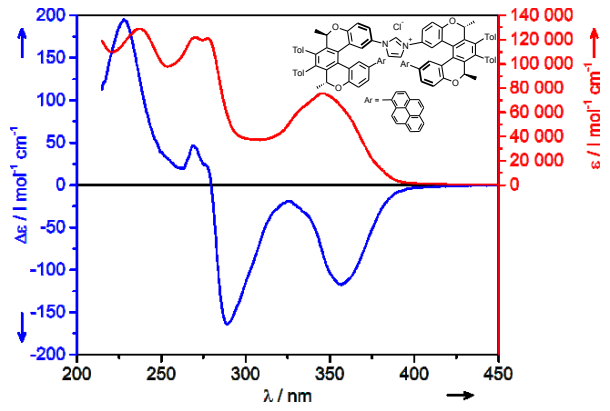
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**180d**



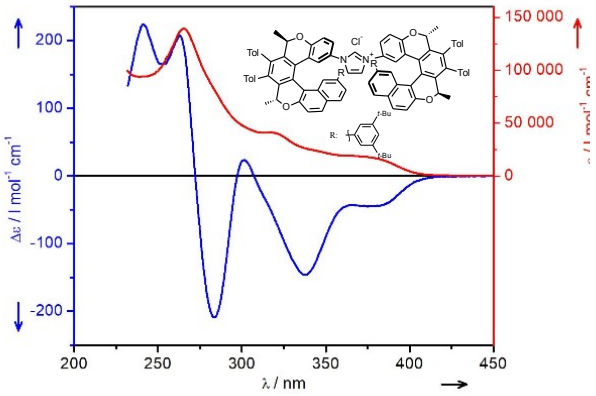
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**180e**



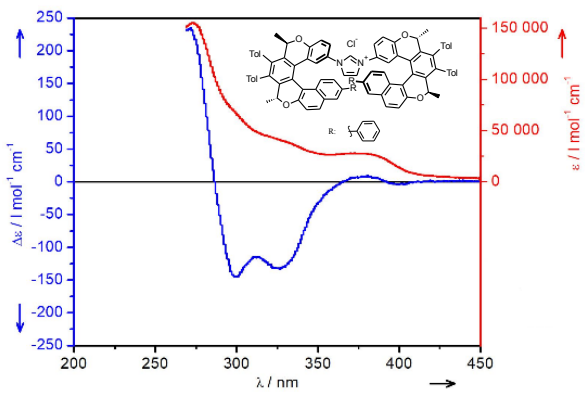
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**180f**



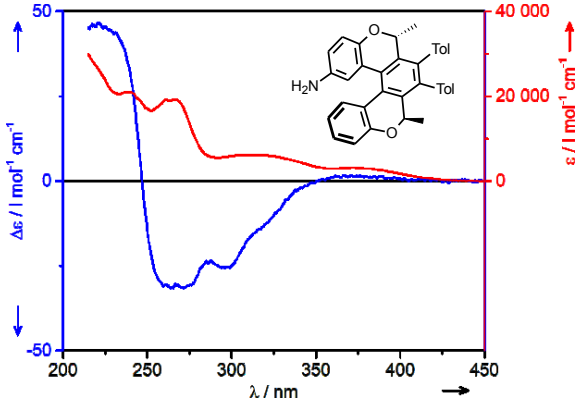
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**208**



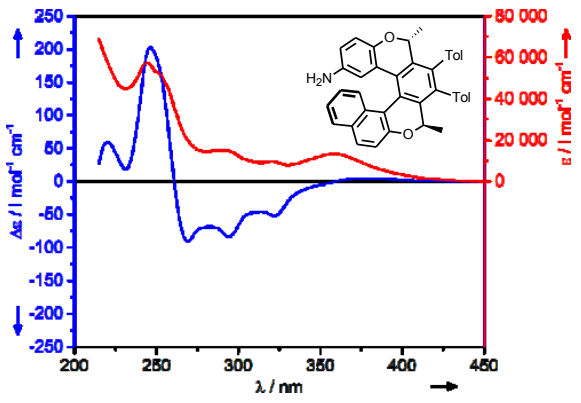
(–)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**207**



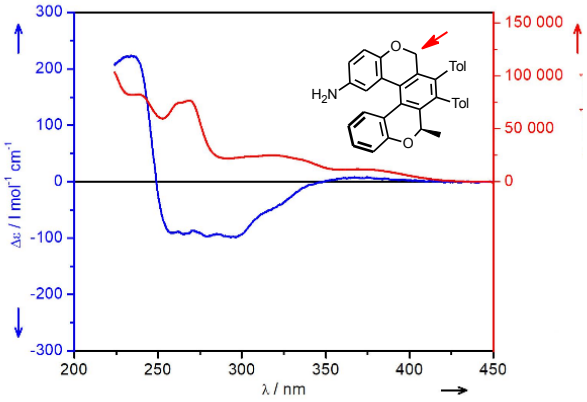
(–)-(*M*,*R*,*R*)-**134**



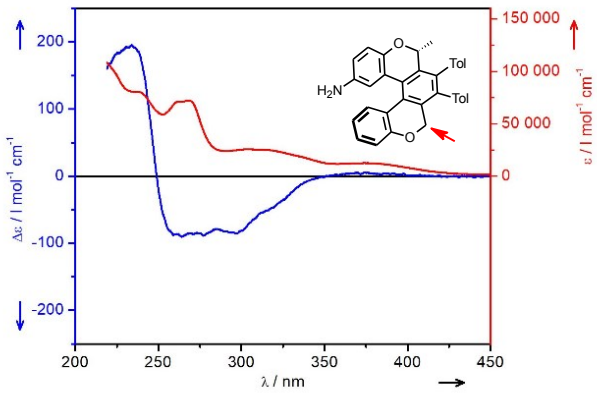
(–)-(*M*,*R*,*R*)-**135**



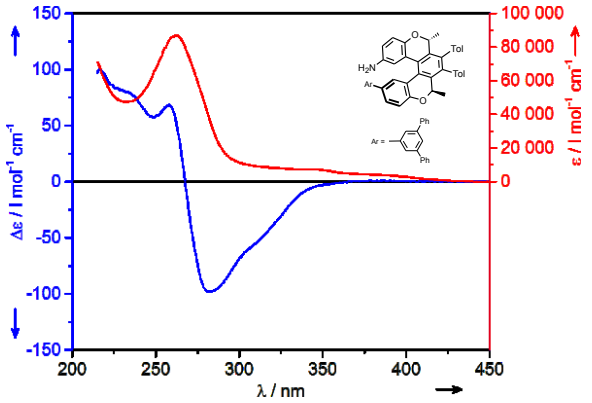
(–)-(*M*,*R*)-**166**



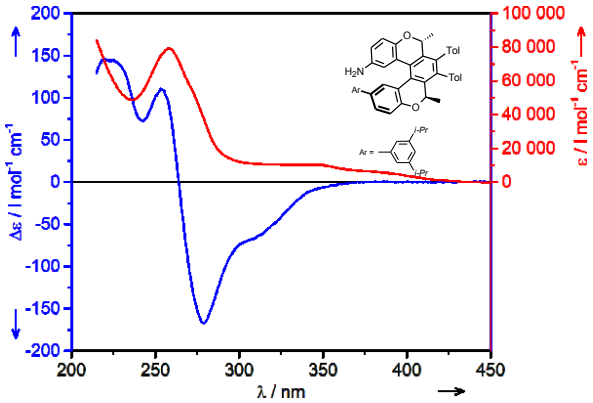
(–)-(*M*,*R*)-**167**



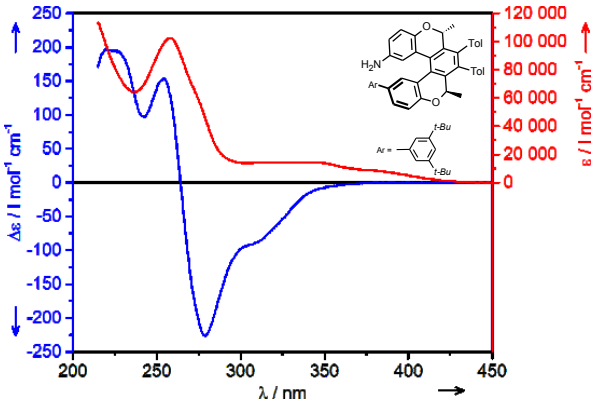
(–)-(*M*,*R*,*R*)-**179a**



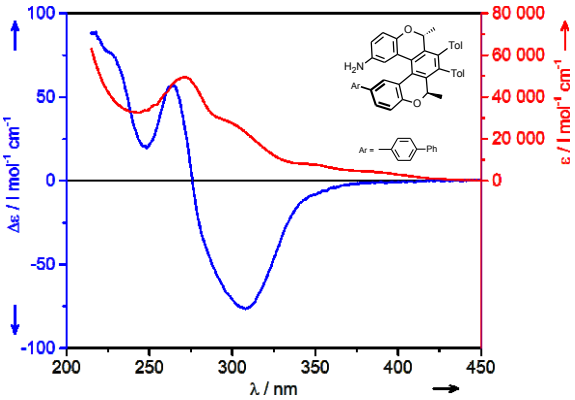
(–)-(*M*,*R*,*R*)-**179b**



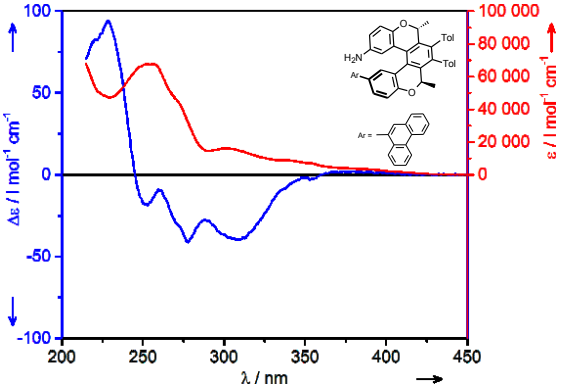
(–)-(*M*,*R*,*R*)-**179c**



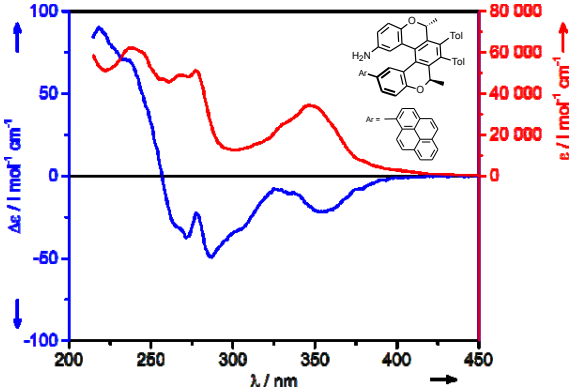
(–)-(*M*,*R*,*R*)-**179d**



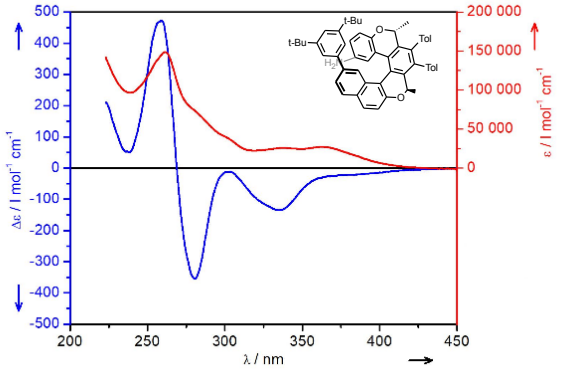
(–)-(*M*,*R*,*R*)-**179e**



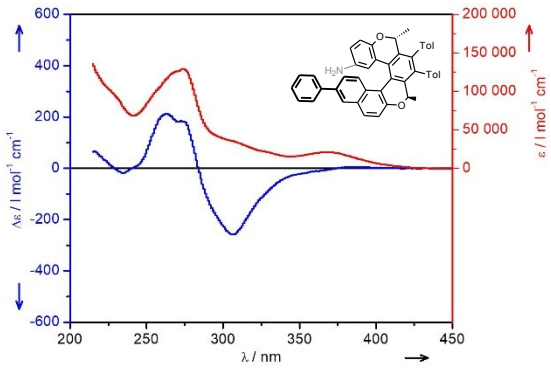
(–)-(*M*,*R*,*R*)-**179f**



(–)-(*M*,*R*,*R*)-**194**



(–)-(*M*,*R*,*R*)-**206**



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